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*Journal*

SEP 27 '61

VOLUME 22, NUMBER 4

AUGUST 1961



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# Medicolegal Aspects of Disaster Operations

ALVIN F. MEYER, Jr., PE, and HUGH B. MITCHELL, M.D.

*Office of the Surgeon, Headquarters Strategic Air Command, Offutt Air Force Base, Nebraska*

Potential medicolegal problems in disaster response operations appear insufficiently realized by many people who may be ultimately concerned. This article, written in working language and developed from actual working experience, attempts to point out problem areas and to offer simple solutions to minimize and prevent medicolegal involvement in emergency response. As background, and for clearer understanding, a classification and a categorizing of disasters are offered, as well as a discussion of ways and means of legal liability and claim, to include types of injury and damage expected. Particular stress is given the recommendations, notably the distinction and importance of accumulation of positive and negative evidence.

## Introduction

THERE are certain aspects of disaster response operations that are little known or studied by those who may ultimately be deeply concerned. Prime among these may be classed the medicolegal aspects. The rising number of malpractice and related suits has stimulated a great deal of interest and concern in selected medicolegal problems but, admittedly, this has predominantly involved situations and potentials inherent in everyday practices or duties. In reality, little thought, particularly in advance, has been given the possible liabilities that may be incurred during the course of an emergency and the response to this emergency.

While the authors are neither legal authorities talented in medical matters nor USAF medical service personnel skilled in the law, the following remarks represent a compilation of working level data on this subject that have been developed from thorough study and a significant amount of actual experience.

Primarily because the authors are career USAF Medical Service personnel this experience has been derived from events concerning the Air Force, particularly the Strategic Air Command. While the material to follow primarily reflects this orientation, the thoughts and principles, with little if any modification, can be adapted to meet any disaster situation or any involved group.

The material presented in this paper is the opinion of the authors and should not be construed as reflecting official Air Force policy.

Presented at the Twenty-second Annual Meeting of the American Industrial Hygiene Association, Detroit, Michigan, April, 1961.

## Classification of Disasters

First, to insure mutual understanding, the basic constitution of a disaster must be established.

Unfortunately, the classifying and even the definition of disaster can be difficult. To different individuals or groups there can be marked differences in opinion and feeling. While most will accept that any sudden unexpected event producing major physical damage and resulting in casualties, or creating a situation capable of destroying life or resources for survival may be considered a disaster, there are extreme variances in classifications. To one person or group a single casualty may be profound, while to others it may take dozens or hundreds of killed or injured to mean the same thing.

To the majority, however, more than 5 or 6 casualties bespeaks a major disaster, yet outside of wars, large scale disasters have been relatively the exception rather than the rule. The Texas City explosion,<sup>1</sup> the earthquakes in Morocco and Chile, the Worcester tornado,<sup>2</sup> and certain fires and train or plane crashes are generally thought of as exemplifying truly major disasters. Every person at some time will face a catastrophe and how he classifies it will depend on his own interpretation.

It may be asked, what then is the difference between a disaster, an accident and an incident. Literally speaking, an incident is thought of as a minor occurrence, an accident a more severe one and a disaster even more severe, thus simply a difference in degree. In the present discussion the terms will be used synonymously, implying that incident and accident may be of disastrous proportions, the level of disaster being along the

lines described below. For the purpose at hand the following arbitrary classification is offered.

1. Class I—51 or more casualties
2. Class II—26-50 casualties
3. Class III—11-25 casualties
4. Class IV—1-10 casualties.

In actuality there can be no precise dividing line as has been indicated. As an example, it is reasonable to assume that there probably will be minimal difference between a Class II disaster with 40-50 casualties and a Class I with 50-60. This sort of classification, however, does give a frame of reference and something of hardened grounds with which to work or, at least, to academically describe.

Other factors may play a role and must also be considered in the final analysis. Predominant among these is the magnitude of over-all environmental damage. A large area of business or residential resources may be destroyed, yet no one may die or be hurt; or 100 people may be lost together with only one small building. Each in its own sense may be called a disaster, so that casualties alone do not necessarily make a disaster.

Under this working classification it can be seen that any of the events cited earlier (*i.e.*, Texas City, etc.) would be nominal Class I disasters, and certainly a nuclear attack would be the highest Class I currently conceivable.

For the sake of completeness, disasters may be further and more broadly considered as being wartime or peacetime. Obviously the liabilities incurred during nuclear hostilities would be multitudinous in character, scope and number, yet many would be waived as a source of claims because of the basic circumstances, and most would be a governmental rather than individual responsibility. Even then, claims would probably be one of the last thoughts of a much reduced population struggling for sheer day to day survival and recovery. Therefore, for this discussion attention will be directed only to those situations actual or possible in peacetime.

Now that a reasonable definition and an idea of magnitude has been given to disaster, specific factors relative to its cause can be discussed.

While disasters can be roughly classified by numbers of casualties, the types can be more precisely delineated by using cause as the basis of reference.

#### Causation Categories

##### I. Operational

- a. Fires
- b. Explosives
- c. Vehicular crashes and/or collisions

##### d. Structural collapse

##### e. Miscellaneous

#### II. Natural

- a. Earthquakes
- b. Tornadoes, hurricanes and other acts of weather
- c. Floods
- d. Fires
- e. Miscellaneous

#### III. Civil

- a. Riot
- b. Rebellion
- c. Panic

#### IV. War

While this listing has been made as logical and comprehensive as possible, the inclusion of very rare occurrences is obvious; yet all these have happened in the past and no doubt will happen again at some time in the future. Although included, war will not be part of the present discussion.

Briefly running down these categories, fires under the operational class can be exemplified by the historical Chicago fire of a few dozen years ago, or with smaller scale fires occurring almost daily in our major cities. Explosions are typified by the Texas City disaster, and vehicular crashes and collisions by any number of serious train and airplane accidents. Structural collapse is rarer but can be signified by the collapse of temporary bleachers at the 1960 Indianapolis 500 speedway classic, or by spontaneous collapse of a building, bridge or similar structure. The miscellaneous group includes the balance of possible events, notably falling objects. Examples here might include parts of aircraft, research balloon devices or similar material; even an unarmed atom bomb fell in South Carolina in 1958. All of the factors involved in the operational section may be considered as some form of negligence.

Under natural disturbances the Chilean and Moroccan earthquakes and the Cameron, Louisiana hurricane typify the first two categories. Forest or dwelling fires from lightning or other purely natural causes exemplify the next group; and the Holland flood of 1953,<sup>1</sup> as well as several major United States river floods, typifies the next. Snow slides or avalanches can be considered under the miscellaneous heading.

Civil disorders could include, under riot, any of several race uprisings in the past, or the famed Cairo riot of 1952.<sup>2</sup> The Hungarian rebellion can be an example of the next group or, on a smaller scale, one of several labor strikes or prison rebellions in this country. Panic, probably the rarest of all, can be evidenced by the Orson Welles radio "landing from Mars" episode in the late 1930s.



While the Air Force has its fair share of everyday accidents and, only naturally, a goodly number of aircraft incidents, there is a special type of disaster with which it must contend. This concerns accidents or incidents involving nuclear weapons. With the exception of aircraft crashes with these devices, the incidents generally are minor and usually not of even a Class IV classification. Fortunately, the more serious events, such as those at Lake Charles (Chennault) AFB, near Barksdale AFB, near Hardinsburg, Kentucky, and, more recently, near Goldsboro, North Carolina, have not been greater than Class IV, and casualties have been confined to immediate military personnel.<sup>4</sup>

Thus far missile operations have been attended by a negligible or minimal number of incidents (excluding purely operational failures), and very few of these of serious proportions casualty-wise. A major factor on behalf of this record is the location of the firing ranges and certainly the direction of firing. With these and similar precautions, no real problems are anticipated under current developments.

#### Potential Medicolegal Involvement

It cannot be denied that any disaster situation may in some way carry medicolegal implications. These situations will then invariably involve three distinct categories of "victims" either singly or in any combination.

The first of these is man himself wherein he may be minimally, moderately or severely injured (either physically or mentally) or be killed.

Secondly, his animate property may be damaged or destroyed. This would include all sorts of livestock, pets or other animal accumulations, and also would cover any manner of crop whether intended for commercial or private consumption.

And thirdly, his inanimate property may be damaged, destroyed or otherwise denied. This sort of property can be described by such things as buildings, various pieces of equipment and land itself.

The legal profession has a similar classification, but one with a more technical basis. Their categories are termed personal injury (essentially the same as the above), injury to personal property and injury to real property.<sup>5</sup> Personal property includes all objects of possession both animate and inanimate which do not constitute real property. Real property consists of land, buildings affixed thereto, and the fixtures which are permanently attached and made a part of any building.

However, for those not too conversant with the details and intricacies of the law, the language herein seems more descriptive and understandable, and appears generally better for the over-all purpose intended.

From this sort of classification it would appear that the physician or health and medical professional practitioner would be concerned only with the liability problems involving man, leaving the other categories to the civil engineer, the agriculturist, the veterinarian or similar personnel.

This is not necessarily or usually the case, particularly in the military service, for in actuality, the dividing line is not nearly so concise. Experience has shown that there are significant areas of overlap so that the medical service, especially, may be concerned not only with injuries to the individual person but also to his animals, crops, buildings and other property.

Generally, the physician or closely allied scientist cannot authoritatively evaluate the condition of a building, a piece of equipment, a crop or a section of land. However, he may play an important part in such evaluation if a health hazard is involved or if the property is contaminated with chemical, biological or radiological material.

Although medical service's concern with problems other than man is a particular requirement for groups such as the Air Force, it would be an equal requirement to a large extent in the event of damage arising from many industrial misadventures. In this instance, people and property could be exposed to unusual or uncommon materials in addition to the more ordinary causes of damage. This can be exemplified by a major explosion in a chemical plant in which chemical hazard and effect would be a problem over and above the usual blast and fire effects. This multiple medical service responsibility could even be true on a smaller and more individual scale, particularly when public health standards are or could be violated. For instance, a farmer hauling a pesticide in his pickup truck could have an accident resulting not only in physical injury, but hazardous environmental contamination as well. While the Air Force and other military services, and most industries, have cognizant medical departments to handle their situations, the individual and frequently uninitiated physician or health officer may be deeply involved and the sole professional support in incidents of this scope.

Thus, medical personnel, be they individuals or on special staffs, must realize at the outset that they will have responsibilities in problems other than man alone. Within SAC Disaster

Control Teams, the physician and industrial hygiene engineer work in close harmony before, during and following an incident on such problems as chemical, biological and radiological contamination, relative crop damage and associated livestock or animal involvement. All this is accomplished not only for basic and primary control of the disaster but with regard to actual medicolegal litigation or study, or with a mind to also prevent, forestall, settle or modify governmental liability. These duties are discharged in complete coordination with other representative branches of these teams (Information Office, Judge Advocate, Civil Engineering, Operations Analysis, Disaster Control and Materiel).<sup>5, 6</sup>

It is important to anticipate medicolegal problems whether the interests of the government, an industry, a community, or an individual are to be represented. This is primarily to minimize the impact on the responsible agency, and it definitely should not be approached with the thought or intent to deprive anyone of his rights or due reward.

#### Time Elements

The factor of time helps establish a working categorizing of probable injury or damage; this is particularly true for operational disasters, but may fit other kinds of disaster just as well. The first class of such disturbance has been labeled as primary, and is envisioned as that damage or injury occurring with, by and at the instant of the initial event whether this be a crash, fire, explosion, or whatever the source. This alteration is essentially instantaneous or occurs within a very short time after this initial event. Simply stated, this refers to that injury or damage that is inflicted on people and/or property at the time of the original impact whatever the nature of the accident or disaster might be.

The other class is termed secondary, and denotes that injury or damage caused by and occurring with the emergency responding procedures. Disturbances of this class can be exemplified by crop and livestock damage as the result of vehicular traffic across a field, water or chemical damage during and following the process of firefighting, or an accident involving an ambulance, fire truck or similar vehicle proceeding to the original disaster. Disturbances within this category will obviously occur later in time of the over-all operation, and will be prone to affect otherwise uninvolved people and material perhaps more remote from the accident site. In too many instances, etiological factors within this secondary classification will cause

more problems or trouble than the precipitating event itself.

While not common, it is possible to become liable for damages where the initial or original disaster is no fault of those responding. In other words, secondary injury or damage would be the responsibility of one element, and the primary responsibility of another. This can be best typified by the humanitarian response of say a military or civil unit to a natural disaster which has affected another segment of the community. Although not responsible for the basic event, the responding organization is liable for any damages it causes in this subsequent reaction. Under the circumstances, some leniency might be expected; but one can still get into trouble by just helping out.

The government was recently held liable for damages arising out of attempts to rescue persons in danger at sea. Once a person, agent, organization or government commences to act, whether it be legally required to do so, it is responsible for any damage or injury that is caused by its negligence.

#### Source of Claims

Not all disaster situations will be attended by liability, at least in the sense of this discussion. Obviously with natural disasters one cannot petition Mother Nature for primary damage; and, similarly, civil disturbances usually do not lend themselves to standard methods of approach. Thus, the major source of worry is confined to secondary damages and to the operational category. These may be aptly termed "man-made," and therefrom man will in some way be responsible. In some instances the precise individual or agency may be hidden in the confusion and the subsequent chain of events, but he is there at any rate. In other instances, a multiplicity of agencies may be at fault singly or in combination.

Once a liability-producing event has been generated, the presentation of subsequent claims will arrive from one of two principal factors.<sup>7</sup>

The first of these has been termed *direct causation*. This infers actual injury or damage to man or his property whether it occurs with the primary event or secondarily from the response efforts. The type and extent of disturbance under this meaning naturally will depend on the type and scope of the accident itself, which includes the subsequent emergency measures. These alterations may therefore arise as the result of such precipitants as impact, fire, explosion, or through chemical, corrosive or radiological contamination, all either singly or in

numerous combinations. The magnitude of involvement or its seriousness will fluctuate depending on the characteristics of the incident, the proximity, and to some extent, the duration of exposure.

The second factor is called *indirect causation* and implies a loss, practically speaking, without actual physical damage or injury. This loss may be of time, employment, utilization or service, and may also arise from situations created by either or both the primary event or the secondary response. Legal interpretation of this and the preceding factor vary somewhat in pure technicality, but the intent and understanding seems clearer with the definitions cited above.

Although perhaps not as clearly visualizable as direct causation effects, claims arising under the indirect category are equally as valid and common. In many instances, claims of this nature will be the sole or prime points of contention in subsequent court action. However, technically speaking, in order to recover, the injured party must show that there was an unbroken chain of causation between the wrongful act and said alleged injury.<sup>6</sup> In some cases he must also show that the alleged injury was a foreseeable consequence, this requirement depending on applicable laws which vary from state to state.

Within this meaning the loss sustained usually results from suspicion, fear or apprehension of possible damage, injury or contamination. Although there might not be evident physical or mental injury, a liability could exist for cost of medical examinations to so prove or disprove, as well as for the job time lost to undergo these studies. This can be exemplified by an individual or group of individuals in the immediate disaster scene who sustain no true physical injury or exhibit no objective or subjective signs, yet there is chemical or radiological contamination in the area. Examination and testing, including recompense from time loss thereto, could and frequently is at the expense of the responsible organization.

Similarly, there could possibly be temporary or even permanent loss or denial of land, crops, animals, buildings and equipment merely on the suspicion of damage or contamination. Liability would therefore be established for the time and cost to verify or invalidate this suspicion and for the service lost during this interval. A simple example of this would be in instances where, say, benign smoke from an accident site drifted over a nearby peach orchard which is near the time of harvest. The crop could easily be lost before lack of contamination is positively assured; or

it may be unacceptable at the market for fear of contamination or damage. Another real example would be in the South Carolina atom bomb drop incident where one party contended that, in spite of complete repairability of the physical damage, his land and fixtures thereon had decreased appreciably in value primarily on the basis of fear of radiological or similar contamination. This contention was supported by many local people, including experienced realtors, even though comprehensive scientific evidence was negative for such contamination. However, radiological contamination, or suspicion thereof, was in this instance ruled by the court as not a consideration in determining damages.

Thus, while direct effects of disasters are relatively commonplace and recognizable by even the inexperienced, there exists this subtle field of indirect effects that has to be appreciated by those who will be involved in emergency response. It must be accepted that problems resulting from indirect effects may be more frequent and of greater magnitude than those associated with the more familiar direct causation group.

In certain claims there may be difficulty, at least academically, in establishing a classification of either direct or indirect cause, or there may appear to be a little of both. These usually are relative to human petitioners, although at times animals may be involved. In these cases there may be disturbance of function in an actual physical sense but without history of any direct (or even indirect) contact. In perhaps simpler words, the claim may imply direct effects yet, technically, it appears more to be on an indirect causation basis. Examples of what we mean in this instance would be the development of a functional-type headache syndrome (or similar physiological disturbance) in an individual in the general area of an incident but who was truly remote to the immediate scene. Such a person would not in any way be exposed to primary or secondary effects either directly or indirectly but, simply as a distance witness, develops any of these disturbances in such a relation. Fairly common examples are individuals several blocks or several hundred yards from a serious accident, witness thereto only by sight or hearing, who subsequently claim some malfunction blameable to this accident. These cases are perhaps more common than they are rare, and they predominantly have a fright or neurogenic basis. Loss of animal productivity may be claimed on similar grounds. Generally these claims are more a source of aggravation than of material loss to the defending party; yet many

may be successful since it frequently is difficult to precisely prove their contentions are invalid.

### Prevalence and Effects of Claims

Suits, claims and similar court actions have steadily increased in number, in many instances on bases not experienced or comprehended in the past by most people. To the truly casual observer it would seem that many actions are filed "at the drop of a hat," or on grounds subject to logical question.

Many of these legal contests are eventually dropped or settled out of court with probably the minority actually coming to trial. However, each case regardless of basis or appearance, is important to those involved, and while the defendant may be in the clear or less responsible than pictured, there can still be a definite and sometimes serious loss.

First, and in almost every instance whether tried or not, there is a *financial* loss; this may be only in general expense of the defense, but more often it involves some measure of settlement of the claim. Depending on the basic circumstances, this latter expenditure can easily be of great magnitude for, along with current trends and the rising living costs in general, awards, while based upon the amount of damages caused, are frequently well into the thousands of dollars.

Secondly, and in lieu of or in addition to financial loss, there can be a *loss of prestige*. It is of no real advantage to the defendant, be he an individual or a large organization such as the Air Force, to be or to be found at fault and to suffer the consequences. From this aspect, it is not inconceivable that subsequent public opinion might adversely affect normal business operations or reliability.

Finally, there could be frequently a *loss to daily operations* when key individuals must be absent from their duty in order to testify or otherwise assist in any manner of litigation. To some individuals or organizations this may not be of significant importance, while to others such a generally unscheduled absence may indeed be a burden.

### Selected Recommendations

With all of the foregoing in mind, there are a few recommendations that can be offered. These are:

1. Recognition of the liability potential
2. Maximum care and attention in emergency response
3. Maintenance of exacting records
4. Collection of supporting evidence, both positive and negative.

### Liability Potential

Recognition of this potential has been listed as number one not because it is actually more important than the others, but because such recognition is necessarily foremost or else these others become meaningless. One must know what can happen and how it will happen. This basically means an indoctrination into and understanding of such intricacies, whether under the suggested classification of primary and secondary effects and direct and indirect causation, or whether it be a similar classification or purely technical one.

Continuing awareness of the ways and means of getting legally involved and of the ultimate costs therefrom is the first step in minimizing or even preventing undesirable consequences in the event of disaster. In this respect, the implication should not be taken that any effort should be extended to deprive anyone of his rights. Rather it is meant that thorough education on the over-all problem, coupled with a reasonable state of preparedness, should do much to prevent fault from ever occurring in the first place.

### Maximum Attention

Every agency does its best to prevent the occurrence of any disastrous situation, but when fate circumvents these efforts and an accident occurs, there is little or nothing at the moment than can be accomplished to negate the impact effects. Subsequent to this, however, much can be done to obviate additional harm to the immediate man, his property and his environment.

With full realization of what can happen in the secondary sense, care should be exercised by all elements when responding to avoid further damage or the creation of new situations.

In this regard, simple things as the use of existing roads whenever possible rather than making your own, maintenance of prescribed emergency speed limits, particularly at intersections or over strange or rough terrain and the avoidance of trespassing on uninvolved property without good reason are materially important. Some may say that this could delay or slow emergency efforts, that it might cost a life that otherwise could have been saved. Contrary to this impression, experience has repeatedly shown that in the long run more damage, injury or trouble generally results when these and similar precautions are not taken. It is remarkably true that a few seconds saved in a "straight line" approach never outweigh the value of a careful well planned and executed response effort.

Most authorities agree that the risks to the emergency personnel and the public in a less thoughtful approach is not worthy of the at-



tempted gain. At the same time, this should not imply sluggishness or too slow a response. Certainly most disasters are attended by fire, explosion, chemical contamination and similar hazards that obviously must be immediately contained. Even here a rapid yet careful response is possible and practical. Speed without hastiness is perhaps a good by-word. In reality, all of this, to a great extent, easily boils down to good ordinary common sense.

### Records

Beyond these simple measures to lessen or prevent fault, it is essential that exacting records on the disaster and the response be kept. This can be accomplished in numerous ways, the details of which will not be discussed at this time. Actually, the type will depend greatly on the individual or organization involved. Generally it will be in the form of on-the-scene personal notes or logs that ultimately are incorporated into a consolidated report.

This sort of document is frequently invaluable for a variety of reasons, the use in claim contentions not being the least. Precisely recorded authoritative and authentic chronological reports, usually by specific experts, are formidable evidences to substantiate and evaluate subsequent claims. The use of portable tape recording-dictation machines is a handy and valuable tool for this purpose.

The SAC headquarters and SAC numbered Air Force and base disaster control teams are composed of specialists in many categories, and among these are medical, sanitary and industrial hygiene and civil engineering personnel who are capable of evaluating animate and inanimate damage in the situations to which we respond. Reports of these individuals has and can contribute much to equitable resolution of liability whether it be in or out of court.

### Evidence Collection

Much of these records and reports will be expert personal opinion and observation, but in every possible instance they should be comprehensively supplemented by the accumulation of physical evidence. This may be in the form of samples, photographs, analyses, affidavits and/or any number of special studies. The evidence thus collected may be classed as positive or negative and each is extremely important in its own sense.

Positive evidence of damage or injury is that which clearly and physically defines, describes or denotes alteration of the norm. Medically this may be a picture or description of a burn, a broken limb, or a laceration, a laboratory report or an autopsy protocol. From a health

physics viewpoint it might be in the form of air, soil, water or environmental sample reports, or the documented results of various radiation or chemical detection instruments. From other aspects this may be photographs, descriptions or affidavits relative to land denial by virtue of debris, damaged or destroyed buildings, equipment or livestock, or crop damage as the result of any accident effect.

These are but a few examples of many. Positive evidence relative to inanimate damage is primarily a civil engineering responsibility while that relative to animate damage carries both civil engineering and medical responsibility in varying proportion, although the agriculturist and veterinarian may be consulted when their services are available. Obviously human injury evidences will be the sole responsibility of the medical service. Besides those broadly mentioned earlier, these will be histories, physicals, consultations, and laboratory, x-ray and other special studies. Frequently these will be one-time evaluations, but in many instances they will be repetitive over fluctuating time periods.

A word of caution relative to collection of samples and specimens. Records of this undertaking should be as exact and detailed as possible, being particularly true with respect to the identity of each person who has possession and control of any given sample. To be admissible as evidence, the party offering the specimen or the result of a laboratory test must show the continuity of control and must be in a position to establish positively that the exact sample taken was the one tested.<sup>2</sup>

Securing or establishing negative evidence is equally important and, in many cases, may even be more important than the positive variety. Negative evidence is just what the name implies, a physical representation of the lack of recognizable or detectable damage or injury.

The same evaluations and methods mentioned under the positive evidence class must be accomplished, that is, histories and physicals, laboratory tests, x-ray, soil, air and environmental studies, photographs, etc. For this category, especially, relatively uncommon and perhaps exotic investigations might be indicated to establish proof beyond the shadow of a doubt that damage or injury has not occurred. Examples of these might be delicate and non-routine bio-assays for specific contaminants, whole body counting for radioisotope intake, or sensitive biochemical analyses of environmental specimens.

The importance of the comprehensive collection of negative evidence cannot be overstressed. Without question the effects mani-



fested by positive evidence create obligations that cannot and should not be denied. There can be no debate or shirking in this responsibility, only a careful documentation to forestall abuse of the obligation. On the other hand when no fault exists, the massing of negative evidence is essential to verify this lack of responsibility. Thus, one of the prime purposes of collection of negative evidence is to accumulate impressive data to support the absence of damage, either at the time or in the event of later claim proceedings.

Experience has indicated that one of the greatest deficiencies in most investigations has been the failure to develop sufficient negative evidence. This alone further stresses the importance of its accumulation. In addition, this evidence must be collected at the time since any delay would result in lost opportunity for reliability and meaning.

It is not improbable that claims may be filed which could be partially if not completely neutralized by the proper negative evidence. It is well enough to accept true or even questionable or borderline liabilities, but it is not good policy or business to accept those of outright unsound basis. In many instances, disputes of this character may be a major share of subsequent action, even further attesting to the importance of appropriate assimilation of reliable negative evidence.

Besides its use as a formidable barrier or defense against undue claims, the compilation of negative evidence has other important meaning. Frequently disaster situations are attended by certain potential follow-on hazards, or even a continuation of some primary effects. These might be fire, danger of explosion, or chemical or radiological contamination. Other examples could be cited. Regardless of cause or effect, the surrounding population is naturally subject to fear or even hysteria over such actualities or potentialities. In these instances well documented or proven negative evidence, properly presented, will do much to counter and dispel this sort of public reaction. This is not only a valuable public service, but at the same time, it may be a surprising deterrent to a variety of subsequent claims.

Therefore, and if for no other reason, evidence of this nature should not be hidden or kept from public dissemination. It must and should be made known to all concerned either by personal contact or through broader means. This may be by area broadcasting, through the police or other civil units, or through the local press, radio or TV. The most rapid and widespread method

should be utilized, and it would be wise to use all such methods possible. The Headquarters SAC team has found it prudent to contact the local and frequently the state and U. S. Public Health Service, to present our findings, allow inspections where security permits, and provide evidence and assurance of the lack of hazard or its complete containment. These individuals then can do much to present the facts to the public and offer authoritative reassurance regarding any hazard.

This emphasis on negative evidence in no way is meant to overshadow the importance of that of the positive class. The latter is generally more clear-cut, obvious and more the subject of experience, so that elaboration of its relative details is superfluous at this time.

Along both lines, the SAC Disaster Control Team makes it standard procedure to have a senior officer visit each resident in the vicinity of an accident after the situation has been controlled and evaluated. Maximizing protocol and interest, this individual expresses regret in the name of the Air Force, advises on damage detected, provides assurance regarding present or future hazard and asks if the tenant has noted alterations not found in our survey. The benefit of this procedure is rewarding in its value toward preventing subsequent or more costly claims. There is some question that this procedure could possibly generate claims that otherwise would have remained dormant. This may be true in a minority of instances, but experience with this approach has not demonstrated such a trend, although this experience admittedly is limited. For the present, it is believed that the good will and benefits derived will overshadow the chance of a more adverse result.

With the integrated approach outlined in all previous remarks it is not impossible to effect settlement of certain obvious claims rapidly, almost in a sense of "on-the-spot." This sort of procedure will depend on the urgency of the claim and, particularly for government agencies, on pertinent guiding regulations. This type of settlement can be simply exemplified by the case of loss of an automobile or other vehicle vital to the livelihood of a claimant. Under the circumstances, replacement could be accomplished promptly rather than wait for the usual chain of events. Such settlements are, of course, not the general rule. However, they may be effectuated in those instances where the government has determined they are needed to alleviate undue hardships and the claims have been determined to be valid.

### Conclusion

Naturally the techniques and principles discussed require a well oriented and trained staff which has the maximum in modern equipment and supplies for each phase of the operation. Since most operational disasters concern organizations made up of larger numbers of personnel, it should not be difficult to organize, train, and equip a small corps to cope with these situations when they occur.

Thoughts and actions relative to medicolegal aspects in disaster operations are but one of many phases in such response. They obviously are not the most important, and they may seem trivial in the face of the death and destruction at the immediate scene. Later, however, their prominence will emerge, at which time they probably will not be so trivial. Awareness of this

change is a large step in the capability developed for ultimate resolution of the many associated problems that may and do arise under the circumstances.

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### INDUSTRIAL HYGIENE COURSES

THE PUBLIC HEALTH SERVICE, through its Division of Occupational Health, will conduct a series of related training courses October 9-27, 1961, at the Occupational Health Research and Training Facility, Cincinnati, Ohio. "Industrial Hygiene Engineering," designed for industrial hygienists and engineers in the field of occupational health, and "Industrial Hygiene Chemistry," for chemists and chemical engineers in this field, are given concurrently, October 9-20. Trainees in both courses meet together for the first week for instruction in industrial hygiene and medicine, toxicology, and principles pertaining to the evaluation of the environment. Meeting separately the second week, work for the hygienists covers temperature and humidity measurements, illumination, noise measurement and control, and industrial ventilation; for the chemists, laboratory analyses for lead, free silica, and solvents; and spectroscopy, polarography, x-ray diffraction, electron microscopy, and gas chromatography. Much time in both courses is spent in the laboratory.

A related course, "Ion-Exchange Techniques for Fluorides and Mercury," follows on October 23-27. This course consists of lectures and laboratory exercises on techniques and applications of recently developed ion-exchange methods which provide desired selective separations and enhance performance of final analytical determinations.

Full descriptions of these courses are given in the *Training Program Bulletin* which is available on request. Trainees may register in single or related courses. Applications or requests for information should be addressed to the Chief, Training Program, Robert A. Taft Sanitary Engineering Center, 4676 Columbia Parkway, Cincinnati 26, Ohio, or to a PHS Regional Office.

# Use of Natural Airborne Radioactivity to Evaluate Filters for Alpha Air Sampling

C. L. LINDEKEN

*Lawrence Radiation Laboratory, University of California, Livermore, California*

Using natural airborne radioactivity as a test aerosol, a method is described which is designed to compare the surface collection efficiency of filters used for alpha air monitoring.

## Introduction

A DESIRABLE property of an alpha air-sampling filter is that the collected activity be retained on the filter surface to avoid counting losses due to burial. Most of these filters now in use have been tested with 0.3-micron di-2-ethylhexyl phthalate (DOP) particles (DOP-Smoke Penetration and Air Resistance of Filters, Military Standard 282, Method 102.9.1, May 28, 1956. Government Printing Office, Washington, D. C.). While this test is useful in rating filters for their ability to retain particles of this size, it does not provide adequate information if the filter is to be used for sampling airborne alpha-emitting radioisotopes, because it gives no distinction between surface collection and burial. Depending on the burial depth and the density of the filter, buried alpha emitters may escape detection because of complete energy dissipation within the filter medium. Thus it is seen that in contrast to chemical analysis, where the only requirement for detection is retention, direct alpha counting is only effective for particles collected on or near the filter surface. Accordingly, a test method showing the relative surface collection efficiency of filters would furnish information of considerable value.

In principle, this method should employ an alpha emitter, such as plutonium, generated as an aerosol in the particle size range typical of air-contaminating accidents. However, in addition to the obvious difficulties in selecting a "typical" size, there are many technical problems associated with controlled particle-size generation. In the method described here, use is made of the short-lived natural alpha activity attached to atmospheric dust. This aerosol occurs freely in nature.

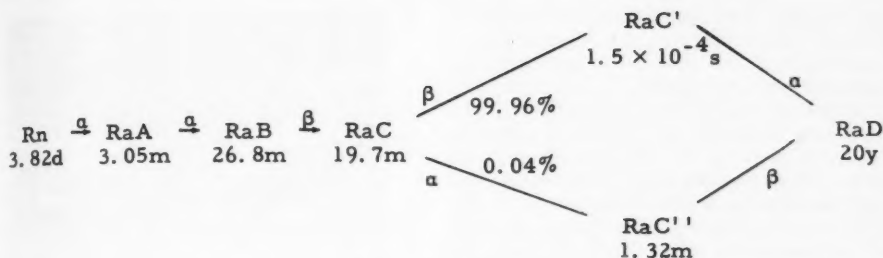
## Natural Airborne Radioactivity

Natural airborne radioactivity originates with uranium and thorium found in varying amounts throughout the surface of the earth. In the radioactive decay scheme of each element a gas is produced—radon from uranium and thoron from thorium. These gases diffuse into the atmosphere where they decay into solid daughter products. Decay schemes for each of these gases are shown diagrammatically in Schemes 1 and 2.

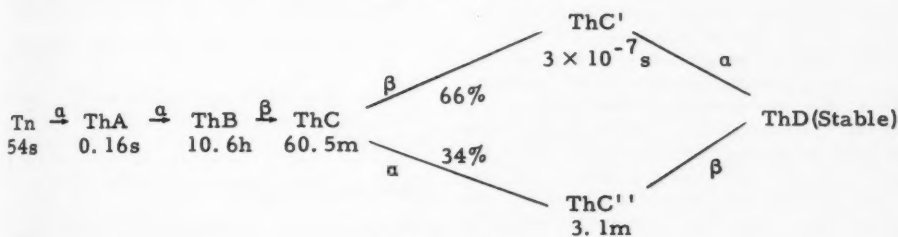
These decay products become attached to airborne dust particles. Each of the decay schemes contains alpha emitters. Consequently if atmospheric dust is collected by filtration, the concentration of airborne radon and thoron daughter products can be determined from the collected alpha activity. The concentration of natural airborne radioactivity varies depending on the geographical area. Within a given area the concentration also varies with changes in meteorological conditions. Diurnal variations are well recognized. Burke and Nolan<sup>1</sup> found that natural airborne activity increased with increases in the concentration of condensation nuclei. They found further that, with an increase in the concentration of the larger less mobile ions, there also was an accompanying increase in intermediate and smaller ions. It may be assumed, therefore, that conditions promoting buildup of large dust particles in the atmosphere may also tend to increase the number of small particles.

From a medical and health physics standpoint, there is interest in the degree of lung retention of particles in the range of 0.001 to 0.1 micron.<sup>2,3</sup> If, as suggested by some of the authorities, these particles are significantly retained in the alveoli, then it is important to know the efficiency of our sampling media for retaining particles in this size range. As the number of atmospheric dust particles in the size

Presented at the Twenty-second Annual Meeting of the American Industrial Hygiene Association, Detroit, Michigan, April 1961.



SCHEME 1. Radon.



SCHEME 2. Thoron.

range of 0.01 micron and less is exceedingly abundant, compared with microscopic sizes, the probability for interaction of decay products with these very small particles is high. Wilkening<sup>4</sup> has found that the major portion of natural activity is present on particles 0.001 to 0.04 micron in diameter. Accordingly, nature may have supplied us with a test aerosol well suited for testing filters for their efficiency in retaining extremely small particles. Its use has appealed to many workers. Carmichael and Tunnicliffe<sup>5</sup> employed natural activity to determine burial losses in an asbestos cellulose paper. They used an electrostatic precipitator as a reference collector. Harley<sup>6</sup> also used natural radon-daughter airborne radioactivity to determine the collection efficiency of aerosol sampling filters, including Whatman 41 and membrane filters. Efficiencies were determined by reference to total activity collected in a static ion chamber. Hasenclever<sup>7</sup> mixed thoron with a dust aerosol of known particle size to produce a radioactive dust. Concentration of thoron daughter products was determined before and after filtration to calculate retention efficiency.

#### Apparatus and Test Method

In the present method, three samples of atmospheric dust are collected simultaneously at the same flow rate. The first sampler contains a Millipore AA filter used as a reference collector. The test filter, operated in parallel, is the second

filter. The third sampler, again using Millipore, follows the test filter in series as a backup. This filter collects activity penetrating the test filter. As alpha activity is collected it is detected by ZnS (Ag) fluors coupled to photomultiplier tubes. Integrated counts are recorded by amplifier scalars. A sketch of the equipment is shown in Figure 1.

Although the filters were originally 47 mm in diameter, they are held in position by a retaining ring which reduces the effective diameter to 42 mm. Fluors are prepared by depositing 10 mg/cm<sup>2</sup> of scintillator on polystyrene plates 2 1/4 inches in diameter by 1/4 inch in thickness. The

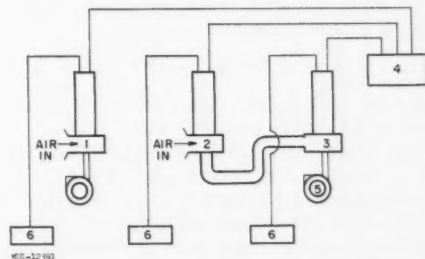


FIGURE 1. Equipment sketch for filter testing:

- (1) Millipore reference filter collector-detector assembly;
- (2) test filter collector-detector assembly;
- (3) Millipore backup filter collector-detector assembly;
- (4) high-voltage power supply;
- (5) Gast pumps;
- (6) amplifier scalars.

scintillator is thermally pressed into the plastic. Distance from fluor surface to filter surface is approximately 0.2 inch. The photomultiplier tube is a 2-in. RCA 6655A coupled to the fluor with Dow Corning QC 2-0057. The photomultiplier tube output is fed through a gain-of-10 pre-amplifier to an amplifier scaler. Figure 2 shows the sample collection-detection assembly.

Sampling periods varied from about 5 minutes to 1 hour, depending on the concentration of airborne activity. As a rule, the sampling time was determined by the time required for the reference filter scaler to collect 1000 to 2000 counts. The instrument background was normally one cpm or less.

By means of bypass valves, flow rates could be selected within the range of 0.5 to 3 cfm. Flow rates were measured at the air inlets using Venturi meters equipped with 0- to 1-in. water Magnehelic gauges. The lower flow limit was established by the accuracy with which the gauge could be read, while the upper limit was determined by the maximum head developed by the Gast 1550 air pump. Venturi meters were calibrated using an 1800-cf/hr dry gas meter. Overall accuracy of the flow measuring system as used was approximately  $\pm 5\%$ . A pressure tap was installed in the test filter assembly, just after the filter, to measure the pressure drop across the filter at the selected flow rate (3 cfm). Correction was made for the pressure drop across the filter assembly itself with only the filter support in place.

Using Millipore AA, it follows that relative to this filter,

$$\frac{\Sigma \text{ counts on test paper} \times 100}{\Sigma \text{ counts on Millipore reference}}$$

$$= \% \text{ of activity collected on test filter surface,}$$

$$\frac{\Sigma \text{ counts on Millipore backup} \times 100}{\Sigma \text{ counts on Millipore reference}}$$

$$= \% \text{ of penetration through test filter,}$$

$$\text{and } 100 - [\% \text{ surface collection} + \% \text{ penetration}] = \% \text{ burial losses within filter.}$$

The above procedure is similar in principle to the one employed by Carmichael and Tunnicliffe. The difference is that the present method detects activity as it is collected and integrates over the collection period. Using this technique, every detectable (counting efficiency is about 35%) disintegrating event occurring during the sampling period is recorded. If counting began after sampling—as in the Carmichael method—the apparent count rate would be lower due to the short half-life of the activity. Thus, for equal

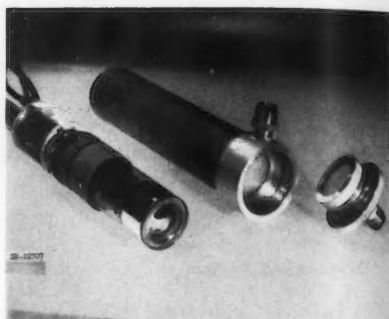


FIGURE 2. Sample collection-detection assembly.

sampling periods, the integration method yields better precision because of improved counting statistics.

### Results and Discussion

Table I shows a comparison between several filters used or proposed for use in alpha air sampling. In all cases these measurements were made at 3.0 cfm, equivalent to a face velocity of 200 fpm.

Data shown in Table I represent averages of several measurements obtained under different concentrations of airborne activity. Variations in surface collection were within  $\pm 10\%$  with no significant correlation with concentration.

It appears that for alpha air monitoring the

TABLE I  
Comparison of Alpha Air-Sampling Papers

Paper	Surface collection %	Penetration %	Burial %	Pressure drop, inches of mercury
Hollingsworth & Vose (HV-70, 9-mil).....	80	2	18	3.0
Hollingsworth & Vose (HV-70 gauze backing, 20-mil, material in roll 3 in. wide, for moving-tape air monitor).....	70	2	28	2.8
Gelman E glass fiber (25-mil).....	89	2	9	1.5
Whatman 41.....	38	22	40	1.6
Whatman Ap/A Polystyrene (30-mil).....	98	2	nil	7.6
Microsaban (Pads of polystyrene sheets; filter was 75 mils thick).....	54	3	43	0.8



glass fiber medium (Gelman E) is superior to the popular HV-70, both with respect to surface collection and flow resistance. While the Whatman polystyrene paper has higher surface retention than glass fiber, it has the disadvantages of high flow resistance and being difficult to handle without shredding. Glass fiber is available in a variety of thicknesses; however, the thinner stocks are too fragile to be serviceable for field use. As might be expected, the surface collection efficiencies for the two HV-70 papers (9-mil and 20-mil) show greater burial in the thicker paper. Final choice of filter media must depend on a balance between the factors of surface collection, flow resistance, and ease of handling.

#### Collection Efficiency of Millipore AA

The Millipore AA paper is used in the test procedure merely to normalize all measurements to a single reference. As such, filters are compared one to another with respect to surface collection, but always relative to Millipore AA. The only requirements of the reference filter then are that it have relatively high surface retentivity for the test aerosol employed, and that it be reproducible in performance.

It is recognized that Millipore AA paper does not collect all the natural activity available from atmospheric dust. In fact, Fitzgerald and Detwiler<sup>8</sup> found that the optimum size for penetration through Millipore AA was in the size range of 0.01 micron, the same general range in which Wilkening found most of the natural radioactivity. However, since we have found no reference filter significantly superior to the Millipore product in surface collection, we have chosen this filter as a point of reference.

#### Comparison of Data: Natural Activity Measurements versus DOP

The method just described is designed to determine relative surface collection efficiencies of filter media. It is of interest, however, to compare filter penetration data obtained using this method with the 0.3- $\mu$  DOP method. Such a comparison is shown in Table II. DOP data are based on the work of Smith and Suprenant.<sup>9</sup> The equipment (Figure 1) could not be operated accurately at the lower velocities; accordingly, a closed-shell sample holder using larger sections of filter paper was placed in series with the Millipore backup filter. Otherwise the procedure was the same.

Retention of aerosols by a filter is due to several forces: impaction (inertial separation), interception, electrostatic forces, and diffusion.

La Mer has discussed these factors in some detail.<sup>10</sup> For our present purpose it is sufficient to note that:

- (1) The size of atmospheric dust particles carrying the majority of natural airborne activity is about one-tenth the size of the DOP aerosol.
- (2) Diffusional separation is more effective for small particles and is greater at low velocities, since the slower the aerosol passes through the filter the more time the particle will have for diffusion away from the air streamline.
- (3) Retention by impaction increases with particle size and velocity.

From Table II it is seen that the deviation between the two methods is greatest for filters such as glass fiber, which show high efficiency for retaining 0.3- $\mu$  DOP. Penetration of natural activity through this medium appears to be independent of velocity. However, because of the small amount of activity collected on the backup filter, the statistical errors are too large to confirm this observation.

Medium efficiency filters such as HV-70 show good agreement at low velocities. At higher velocities, when separation of 0.3- $\mu$  DOP is influenced by the impaction mechanism, the agreement deteriorates.

Whatman 41, which shows relatively low efficiency for retaining either size aerosol, clearly indicates that the penetration of both natural activity and DOP is velocity dependent. Figure 3 shows the penetration-vs-velocity curve for

TABLE II  
Comparison of Penetration Measurements,  
Natural Airborne Activity vs 0.3- $\mu$  DOP.

Filter medium	Velocity, ft/min	Penetration %	
		Natural activity	0.3- $\mu$ DOP
Glass fiber	20	2	0.04
	150	—	0.01
	200	2	—
HV-70	20	4	3.5
	150	—	0.1
	200	2	—
Whatman 41	5	—	89
	6.5	29	—
	20	42	77
	50	48	67
	100	—	44
	116	32	—
	150	—	29
	200	22	15

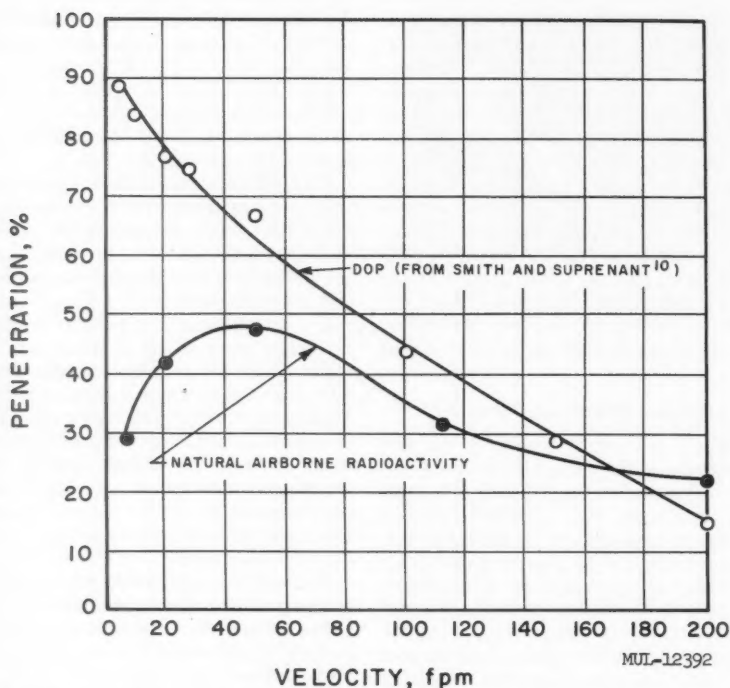


FIGURE 3. Penetration vs velocity, 0.3- $\mu$  DOP and natural airborne radioactivity through Whatman 41 filter paper.

Whatman 41 using natural activity and DOP. Separation of 0.3- $\mu$  particles by diffusional forces is not apparent in this medium at the velocities employed by Smith and Suprenant. As the penetration of DOP constantly decreases with increased velocity, this suggests that impaction is the principal factor involved. It appears, however, that diffusional separation has a strong influence on particles of the size carrying natural activity, as evidenced by the maximum in the natural activity curve. Because of their small size, this influence is exerted over a wide velocity range. Impaction is also involved, but becomes predominant at higher velocities than is the case with larger particles.

At low velocities it would appear that Whatman 41 retains small particles better than 0.3- $\mu$  particles. At 200 fpm, the penetration data between the two methods are in close agreement. For those who use Whatman 41 for atmospheric sampling, these results suggest an additional argument for higher face velocities. Not only is retention of 0.3- $\mu$  particles reasonably good at 200 fpm, but also it appears that very small particles are better retained at this velocity.

### Summary

A method has been described using natural airborne radioactivity as a test aerosol, which is designed to compare the surface collection efficiency of filters used in alpha air sampling. Of the filters tested it appears that glass fiber is superior to HV-70. Thin sheet polystyrene filters, although superior to glass in surface collection, have the dual disadvantage of high resistance to flow and handling difficulty due to shredding.

Although the method lacks the accuracy desirable in a reference procedure for penetration measurements, it does provide a screening technique for new filters for which DOP data are lacking.

Data are presented for Whatman 41 paper which show that the retention of particles in the size range associated with natural activity is quite velocity-dependent. A maximum occurs in the penetration-vs-velocity curve showing that both diffusion and impaction separation mechanisms are involved. At low velocity ( $\approx 5$  fpm), Whatman 41 retains natural activity with

greater efficiency than 0.3- $\mu$  DOP particles. At 200 fpm, retentions for both particle-size ranges are in close agreement.

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#### AIR POLLUTION LIBRARY INDEX

THE BAY AREA AIR POLLUTION CONTROL DISTRICT established its technical library and this specialized index in 1956-57 to serve the District staff and others who have air pollution problems in the Bay Area. More than 8,000 technical reports and other publications on air pollution and its control have been extensively cross-indexed for rapid search and retrieval. This index now consists of 16,850 reference cards. It is the most comprehensive index on this subject and is currently valued at \$50,000.

Complete copies of the index have been purchased by the United States Public Health Service, Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio, and by the New York State Air Pollution Control Board, Albany, New York. Additional sets are available and are offered to others at prices ranging from \$2,000 to \$2,800 depending on the special features desired. The indexes are kept up-to-date by semi-annual shipments of the additional cards at a charge of about \$250 per year to the subscriber.

Requests for further information are welcome and should be addressed to: BENJAMIN LINSKY, Air Pollution Control Officer, Bay Area Air Pollution Control District, 1480 Mission Street, San Francisco 3, California.

# The Estimation of Areas within Isopleths of Dosage Downwind of a Point Source

WILLIAM P. ELLIOTT, Ph.D., and PAUL W. NICKOLA, B.S.

*Geophysics Research Directorate, U. S. Air Force Cambridge Research Laboratories, Bedford, Massachusetts, and Hanford Laboratories Operation, General Electric Company, Richland, Washington*

A method is presented for estimating the area enclosed by an isopleth of dosage downwind of a point source in the atmosphere. The method employs an empirical relationship between the area enclosed by a dosage isopleth and the value of the isopleth divided by the source strength and multiplied by wind speed. The relationship is classified according to atmospheric stability. Comparisons are made between results obtained over short grass (O'Neill, Nebraska) and arid sagebrush vegetation (Hanford, Washington).

## Introduction

THE purpose of this paper is to present a method of estimating the horizontal area downwind of a point source of pollution which will be subjected to a dosage equal to or greater than some previously selected value. The discussion is based upon some results of recent diffusion experiments conducted under the joint sponsorship of the Air Force Cambridge Research Laboratories and the Atomic Energy Commission. In addition, the results will be compared with the results of a similar analysis performed by one of the Authors<sup>1</sup> on another set of diffusion experiments conducted by the Air Force Cambridge Research Laboratories in 1956. Throughout this paper experiments will be referred to by their nicknames, Green Glow (GG) and Prairie Grass (PG). In the next few paragraphs these experiments will be briefly discussed.

## Project Prairie Grass

Project Prairie Grass was conducted during the summer of 1956 near O'Neill, Nebraska. The local area was quite flat and covered with short grass a few inches high. A network of samplers was laid out in concentric semi-circles with each sampler 1.5 meters above the ground. The semi-circles had radii of 50, 100, 200, 400, and 800 meters with the source of tracer material located at the center. The tracer was sulfur dioxide emitted continuously from a point source 46 cm above the ground (except for four releases made at a height of 150 cm). In all, 68 gas releases were made during this program about half

being at night. In addition to the horizontal sampling, vertical sampling was obtained from five towers located 100 meters from the source.

Also measured were such meteorological parameters as vertical wind and temperature distributions, for one of the primary aims of the program was the correlation of the observed diffusion patterns with ambient meteorological conditions. A full discussion of this program as well as the data has been given by Barad.<sup>2</sup>

## Project Green Glow

This project was a direct outgrowth of PG where the attempt was made to extend the results of PG to greater distances. Most of the attention of this paper will be focused on the results of this program.

The experiments were conducted during the summer of 1959 at the Hanford Reservation of the Atomic Energy Commission in southeastern Washington. The program was planned by personnel of the Geophysics Research Directorate, Air Force Cambridge Research Laboratories and the Hanford Laboratories Operation, Hanford Atomic Products Operation, General Electric Company. Besides these groups, personnel from the Texas A&M Research Foundation and 6th Weather Squadron, 4th Weather Group, Air Weather Service participated in the actual program.

Because of the greater distances involved, and hence the need for greater source strengths, a tracer other than  $\text{SO}_2$  had to be used. Fluorescent zinc sulfide particles (U. S. Radium Corp. No. 2210) with a geometric mean particle di-

ameter of about 2.5 microns was chosen. This pigment was suspended in a tank of water and this suspension was emitted for about 30 minutes from two insecticide applicators placed on the ground. Between 0.8 and 3.6 kg of pigment were emitted during each run. Because the pigment had to clear nearby sage brush the nozzles were pointed upward. This gave an effective source height of about 10 feet. The pigment was collected on membrane filters about two inches in diameter. These filters were placed along segments of six circular arcs at various distances from the source. The distances between samplers were 2° along the 1/8 and 1/2 mile arcs, 1° along the 1 and 2 mile arcs, 1/2° along the 8 mile arc, and 1/4° along the 16 mile arc. Additionally, vertical samples were taken on 5 towers on each of the 4 arcs closest to the source. However, all samples considered in plotting dosages for this paper were collected at an elevation of 1.5 meters.

Air was drawn through these filters at various flow rates depending upon the distance from the source. At the 8 and 16 mile arcs the high flow rate, coupled with the long exposures, resulted in the collection of considerable foreign matter along with the pigment and increasing the difficulties in the assaying technique.

The technique for filters relatively free of foreign matter consisted of activating the zinc sulfide particles on the filters by a fixed-strength source of plutonium alpha particles and counting the resulting scintillations with a multiplier photo tube.<sup>3</sup> For the 'dirty' filters and for calibrating the assaying technique described above, the filters were dissolved, exposed to white light and the resulting phosphorescence measured in an automatic liquid scintillation counter whose readings could be converted directly to mass.<sup>4</sup> A correction factor for the effect of foreign matter in the sample was determined from turbidity measurements with a colorimeter. Because of the foreign matter the values of dosage obtained for the furthest two arcs are not quite so accurate as the values obtained for the inner arcs. The standard errors of the values of dosage for the inner arcs are almost all below 10% and many are below 5%; for the outer two arcs the standard error is about 21%.

The terrain of the Hanford Reservation, while generally flat, contains more surface irregularities than the site of the PG experiments. The surface is covered with desert grass and sage brush, the latter often growing to heights of 4 or 5 feet and averaging about 3 feet high.

Further details of the program will be found in a forthcoming paper.

### Method of Analysis

The method used to determine the area enclosed by a given value of dosage in this study is the same as that employed by Elliott<sup>1</sup> in the study of PG data. Dosage (D) here is defined as the mass of tracer collected divided by the flow rate through the collector, and has the units of gram-seconds per cubic meter. These values were plotted at each observation point on a grid proportional to the actual sampling grid. For the GG data these values were plotted for 18 of the 27 gas releases made. The other nine releases were not used for a variety of reasons, the most common being failure of the pigment to remain within the sampling network during the experiment.

After the values of dosage were plotted, the highest values observed on selected arcs were determined and isopleths (lines of equal value) were drawn on the grid. The arcs selected for the PG experiments were 800, 400, and 200 meters from the source and for the GG experiments the arcs were 16, 8, 2, and 1 mile from the source. The areas within these isopleths were then measured with a planimeter. Figure 1 shows a typical pattern obtained for the peak dosage at 16 miles. (The sampling network and general terrain of the Hanford Reservation are also shown in Figure 1. The contour lines are 100 ft intervals.) Obviously a certain amount of subjectivity enters into the drawing of the isopleths. However, a check made by having several people draw the lines independently of one another gave areas in agreement within 20% and many differed by only a few per cent.

Since differing amounts of pigment were released during different runs, observed values of the peak dosage were divided by the total amount of pigment emitted (E). Further, it had been found during the analysis of the PG data that the inclusion of a representative wind speed in the final prediction scheme resulted in significant improvement. Therefore, the values of D/E were multiplied by the wind speed (U) observed at 16 meters above the ground. Finally the values of DU/E were plotted against the values of area (A) enclosed by the observed value of  $\frac{DU}{E}$  on logarithmic paper.

This way of representing the data, i.e., plotting  $\log A$  vs  $\log \frac{DU}{E}$ , is not arbitrary but is suggested by consideration of some theoretical results derived by Sutton.<sup>5</sup> Elliott<sup>1</sup> found that when PG data were similarly plotted the points tended to fall along a straight line. Since the



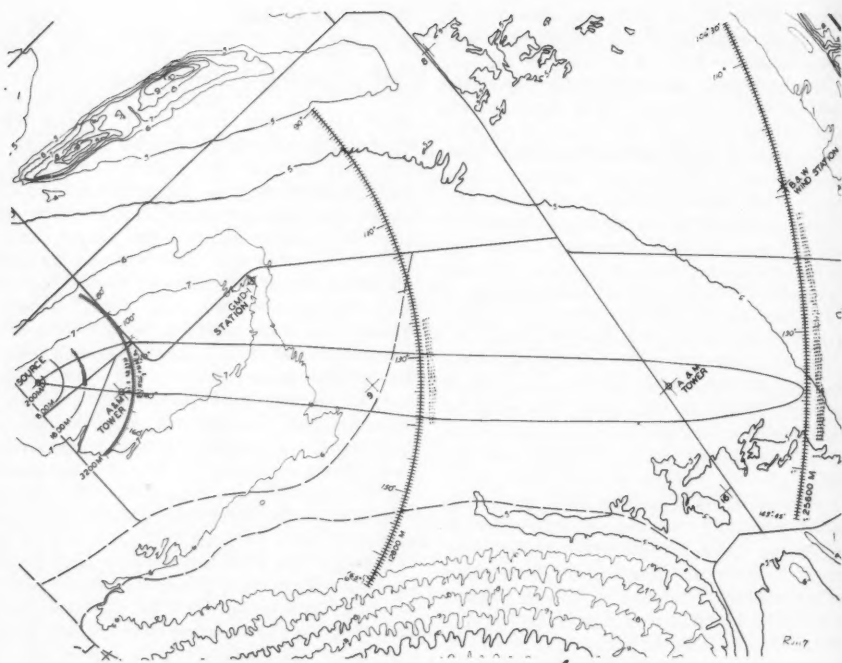


FIGURE 1. Typical isopleth of peak dosage 16 miles from source.

PG data only extended about  $\frac{1}{2}$  mile from the source, one of the main interests of this study was to see if the straight line relationship would hold out to distances of 16 miles.

It should be mentioned that the choice of the wind speed at 16 meters is somewhat arbitrary; for most cases the wind speed at some lower height would have served as well. However, because the height of vegetation at the two different sites (GG and PG) differed considerably, it was deemed appropriate to choose a height sufficiently far above the surface that the effects of these differences would be minimized. Also, of course, the specific height was dictated by the location of anemometers at the two sites.

Another physical parameter which is of frequent concern in diffusion studies is the atmospheric stability. The next few paragraphs will briefly discuss the general effects of stability on diffusion processes for the reader who may not be familiar with them.

When the air temperature increases with height (inversion) the atmosphere is called "stable". When the air temperature decreases with height (lapse) the atmosphere is called "unstable". As these two terms imply, mixing

is inhibited during stable conditions and enhanced during unstable conditions relative to the condition of neutral thermal stability, where there is no change of temperature with height. In general, unstable conditions are typical of the daytime and stable conditions typical of the nighttime.

In addition to the vertical temperature gradient, the vertical wind speed gradient affects the dispersion of a pollutant. Other things being the same, a pollutant will disperse more rapidly when the wind speed changes rapidly with height than when the wind speed changes only slowly with height. These two factors, the vertical change of temperature and wind speed, can be combined to give a quantitative measure of the atmospheric stability.

There are many such combinations depending upon the height interval chosen over which to measure the vertical gradients. In this particular study the stability ratio, defined as the temperature at 4.0 meters minus the temperature at 0.5 meters divided by the wind speed squared at 2.0 meters, was used. (Several other definitions of stability were checked and the results were not materially different.) Positive values of

stability ratio indicate stable conditions, the larger the numerical value the greater is mixing inhibited; negative values indicate unstable condition, the larger the absolute value the greater is mixing enhanced. Since all GG observations were made at night the stability was always positive during these observations.

# Results

As mentioned above when the area (A) was plotted on logarithmic paper against  $\frac{DU}{E}$ , the points tended to fall along a straight line. Furthermore, when the PG data were put into separate classes depending upon the value of stability ratio appropriate for the period of emission, the points in each class tended to follow straight lines distinct from one another. In other words, the relationship between  $\frac{DU}{E}$  and A depended upon stability. Not surprisingly this same tendency was found in the GG data. Figures 2 and 3 show the results of these plots for the data divided into two stability classes. Figure 2 shows the data for the least stable class and Figure 3 shows the data for the most stable class. If the temperature is in degrees Celsius and the wind speed in meters/sec, a natural division of the data occurs at a value of stability

ratio of 0.06 and this value was taken as the dividing line between the two classes. The solid line in both graphs is the line of best fit, as determined from a least-squares analysis, for the GG data, and the dashed line is the line of best fit for the PG data. The equations of these lines are as follows:

GG data, least stable

$$A = 4.0 \left( \frac{DU}{E} \right)^{-1.09} \quad (1)$$

GG data, most stable

$$A = 75 \left( \frac{DU}{E} \right)^{-0.88} \quad (2)$$

PG data, least stable

$$A = 25 \left( \frac{DU}{E} \right)^{-0.98} \quad (3)$$

PG data, most stable

$$A = 91 \left( \frac{DU}{E} \right)^{-0.92} \quad (4)$$

When one compares the exponents of the equations or the slopes of the lines on the graphs (which are the same quantities) one can see that

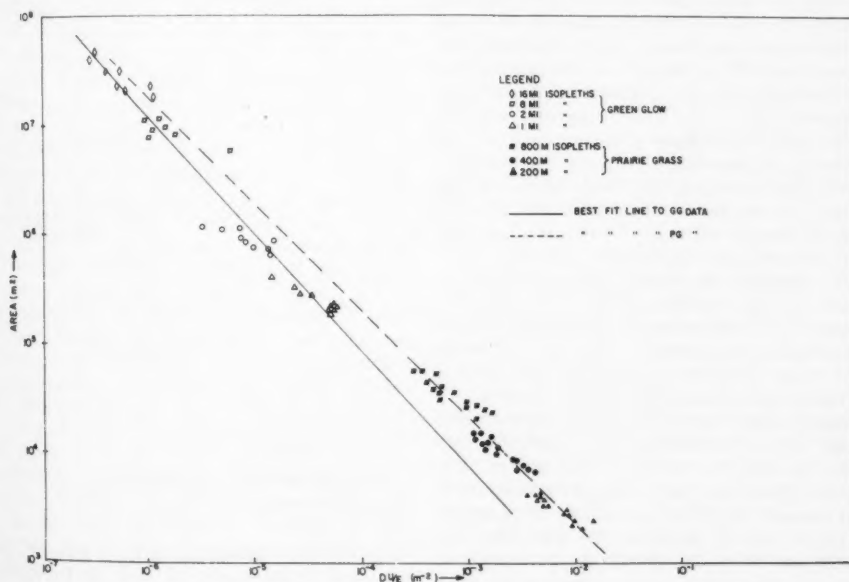


FIGURE 2. Area vs.  $\frac{DU}{E}$  from GG and PG data for least stable cases (stability ratio less than 0.06).

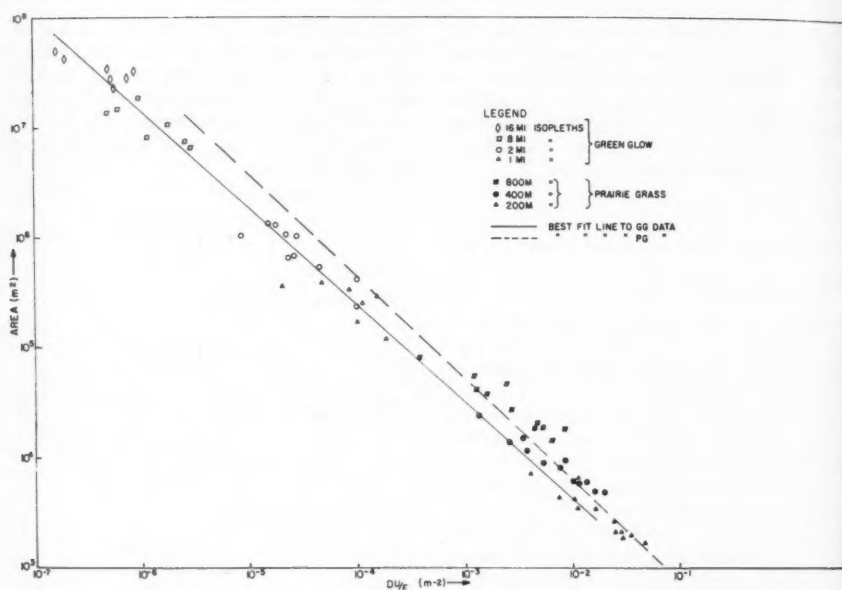


FIGURE 3. Area vs.  $DU/E$  from GG and PG data for most stable cases (stability ratio greater than 0.06).

there are but slight differences between PG and GG for the same stability class. In fact no statistical difference between these slopes can be demonstrated. This result is encouraging in view of differences in terrain, vegetation, tracer material and travel times to the samplers between the two sets of experiments.

It is also apparent from the two figures that the GG lines are not simple extensions of the PG lines. If one were to have used the extrapolated PG lines to estimate the area enclosed by a given isopleth during the GG program a consistent overestimate would have occurred. A possible reason for this can be found by considering the data from towers. In almost all cases the maximum concentration of tracer was found at the lowest elevation (0.5 m) measured at PG and the values at 1.5 m (which was the measuring height used in determining  $D$ ) were usually at least 90% of the value at 0.5 m. However, due, in part at least, to the elevated source at GG, the maximum values were frequently well above the 1.5 level. Figure 4 is a schematic illustration of an isopleth of  $D$  for this case. The elevation view shows the pattern in the crosswind plane. The solid curve is the isopleth under consideration. The line AB represents the intersection of the plane of the maximum concentration with the crosswind plane and the line CD

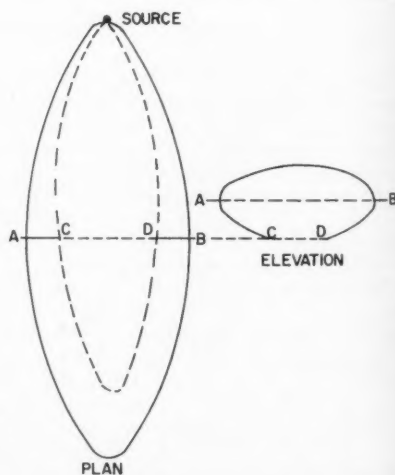


FIGURE 4. Schematic illustration of an isopleth of  $D$  in the vertical and horizontal planes.

represents the intersection of the horizontal plane 1.5 meters above ground with the crosswind plane. Obviously, the width of the isopleth in the plane of the maximum is greater than the width in the 1.5 m plane. The dashed line in

the plan view is the isopleth drawn in the 1.5 m plane and the solid line is the isopleth in the plane of the maximum value of D.

This drawing is based upon the results of the data taken on the towers. (The fact that the towers define a cylindrical surface rather than a plane is of no consequence to the argument.) While the tower data are not sufficiently dense to permit the accurate drawing of the isopleths in the plane of the maximum, they are sufficient to indicate that Figure 4 is a qualitatively realistic picture. This picture indicates that the value of area determined from observations in the 1.5 meter plane would be a good bit less than the area drawn in the plane of the maximum.

The tower data also indicate that the picture is more complex than this simple illustration shows. In many cases the plane of the maximum was not parallel to the ground plane but increased with height downwind. Also, the plane frequently tilted upward to the right looking downwind, *i.e.*, the line AB was not parallel to line CD in the elevation view. It does not appear that this picture is unique to the GG experiments. It is quite probable that similar difficulties would be encountered with any set of observations of diffusion over long distances.

While the above discussion indicates that one would expect different area-dosage relationships at GG and PG, it is not possible to determine if this picture accounts completely for the overestimate of the GG areas by the PG results. Differences in terrain, vegetation, or deposition rate are other factors which may significantly affect the area-dosage relationship. But the fact that best-fit lines for the two sets of data are almost parallel does suggest that the results are comparable and that the PG lines can be extrapolated for much greater distances as long as the observations are made near the plane of the maximum concentration.

As mentioned above the GG data tended to be divided into two separate classes depending on the value of stability ratio. Strictly speaking this statement is true only for the data derived from the peak dosages at 1 and 2 miles. If Figures 2 and 3 were superimposed it would be seen that almost no separation by stability is found for the areas enclosed by the peak dosages at 8 and 16 miles and that the lines of best fit for the GG data converge. If this result is real (*i.e.*, not simply due the greater difficulty in determining the observed dosage caused by the dust on these filters or of the particular terrain) then it indicates, during stable conditions at least, that at great distances from the source stability is no longer a factor in delineating the

area-dosage relationship (and possibly not a factor in determining the downwind variation of concentration at these distances).

One further point to emphasize is the shape of the isopleths. The very elongated elliptical shape indicated in Figure 1 is typical of those patterns occurring at GG and at PG during stable conditions. The maximum width occurs about halfway between the source and the maximum distance from the source. Very roughly, the maximum width is about  $1/10$ – $1/20$  of the maximum length. The slight curvature of the whole plume indicated in Figure 1 is the result of shifts in wind direction occurring during the observation period. Releases made during unstable conditions (daytime) at PG showed less regularity and it was frequently found that isopleths appeared fan-shaped rather than elliptical. Although the longer emission time at GG would tend to reduce the fanning out of the area one would expect less regularity in the shape of the area during the daytime than was observed at night at GG.

### Summary

This study has shown that the area enclosed by an isopleth of dosage can be represented on logarithmic paper as a linear function of  $DU/E$ . Some separation of the data points by stability class is evident at 1 and 2 miles from the source. When the results of the GG experiments are compared with the results of the PG experiments it is found that the lines representing the best fit to the two sets of data are essentially parallel but are displaced relative to one another. This discrepancy is partially explained on the basis that while the PG data represent areas very close to the plane of the maximum concentration, the areas derived from the GG data appear to be in a plane sufficiently far removed from the maximum plane to produce smaller areas for the same value of  $DU/E$ . The shape of the isopleth is approximated by an elongated ellipse in stable situations but is probably less clearly defined in unstable cases.

It is believed that the results presented here can serve as a useful guide in future studies of this sort. Further observations will be necessary in order to properly define the effects of differences in vegetation and terrain as well as deposition and stability at great distances upon the area-dosage relationship.

### Acknowledgments

Thanks are due Dr. M. L. Barad, of the Air Force Cambridge Research Laboratories, and J. J. Fuquay, of the General Electric Company's

Hanford Atomic Products Operation, for their suggestions and review during the preparation of this study.

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### RESEARCH GRANTS IN RADIOLOGICAL HEALTH

THE U. S. PUBLIC HEALTH SERVICE has announced a special program for research grants in radiological health. These grants are offered to support research by individuals, universities, hospitals, laboratories, and other public or private institutions in the assessment and control of man-made and natural radiation exposures to the individual, no matter how the separate components may originate. Research proposals for grants in this program should contribute to the determination of the extent and character of the radiation problem as well as the mechanisms by which radiation produces damage. Epidemiologic, biologic, physical, and chemical studies aimed at the elucidation of the radiation damage "cause and effect" relationship are essential if low-level and long-term radiation exposure effects are to be accurately assessed and general control programs organized. Studies of the physical and chemical mechanisms attending radiation exposures, the design of equipment, the development of research and assessment techniques, and the development of control devices and procedures are necessary types of projects to advance the entire front of our knowledge of radiation hazards and injuries. The determination of the consequences of radiation exposures for present and future generations will require intensive investigation. Some studies may be conceived to assess the relationship between health hazards created and possible beneficial effects derived from radiation usage.

Projects which can be considered in this grants program extend across the entire gamut of the relationship of radiation to life and man. They may well be as specific as the study of a small change in a certain type of cell or as broad as the "total view" of man's ecological system. For information and application forms please write to: Dr. Paul F. Hahn, Chief, Office of Extramural Grants, Division of Radiological Health, U. S. Public Health Service, Washington 25, D. C.



# Correlation of Industrial Noise Exposures with Audiometric Findings

E. J. SCHNEIDER, A.B., J. E. PETERSON, M.S., H. R. HOYLE, B.S.,  
E. H. ODE, and B. B. HOLDER, M.D.

*Biochemical Research Laboratory, The Dow Chemical Company, Midland, Michigan*

A noise exposure profile system was developed following study of noise exposures and hearing losses among Dow employees. Four categories of severity were established ranging from quiet job (profiled "A") to extremely noisy jobs (profiled "D"). The possible effects and interactions of noise exposure, age, time on the job, previous noise exposure, ear pathology, and the use of ear protection were studied. There was evidence that men working in jobs profiled "A" and "B" showed more hearing loss than was expected for normal ageing. Men in jobs profiled "C" and "D" showed hearing losses greater than those expected from ageing.

## Introduction

WHEN an industrial hearing conservation program is begun several areas of insufficient knowledge become immediately apparent. For instance, do noisy industrial jobs actually cause a significant impairment of hearing, and if so, is hearing loss related to both noise level and duration of exposure? Is there a real need for men working on noisy jobs to wear ear protection in order to avoid hearing loss? If a man shows a significant hearing loss is there justification for moving him to a quieter job regardless of his age? And/or, should men of all ages with varying degrees of hearing impairment be kept from working on noisy jobs?

Some of these questions could be answered in a rather general way from information at hand, but specific answers for specific jobs within The Dow Chemical Company were lacking. Therefore, at the very beginning of a hearing conservation program, an effort was made by all concerned (including personnel from our Medical, Environmental Research and Safety Departments) to gather data designed to help answer these questions.

## Audiometric Examinations

Beginning in 1956, periodic audiometric examinations were made of Dow employees working on jobs known to be noisy. These examinations were conducted with a Peters Audiometer which has continued to be the instrument used for all hearing examinations in the field. The first field work

was done in an audiometric testing booth mounted on an open trailer. This trailer was moved from one location to another as necessary. Because it was difficult, at times, to find locations for the booth which would be quiet, comfortable, and convenient, a house trailer was later purchased to house the audiometric booth. The house trailer has proved to be a completely satisfactory answer to the problem, and its use could even be justified on an economic basis.

As with any type of equipment, periodic maintenance and calibration of the Peters audiometer has been necessary. Such maintenance has included the following:

- (1) Each day the audiometer is used the audiometrician determines his own threshold of hearing for a set frequency. Any change in the results of this test is a signal for maintenance.
- (2) Every six months the audiometer is taken to the Instrument Department where the voltage across the receivers is measured at each test frequency and is compared with the correct values. All electronic tubes are tested at this time.
- (3) The instrument is sent back to the factory for major repairs and overhauls when necessary. This has been done only once since it was purchased.

## Noise Exposure Measurements

Use of this instrument in early 1956 indicated that many of the men tested had significant hearing losses. As soon as this was shown to be the case, a program was initiated to determine the extent of noise exposure associated with various

Presented at the Twenty-second Annual Meeting of the American Industrial Hygiene Association, Detroit, Michigan, April, 1961.

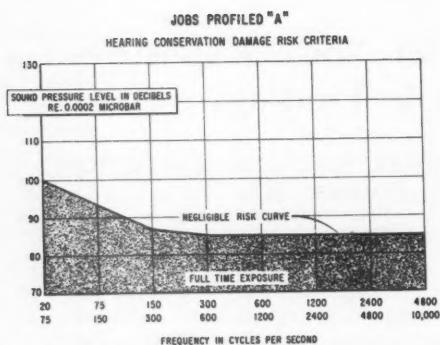


FIGURE 1. Quiet jobs within a quiet department were profiled A.

jobs. In each case, duration of exposure as well as the noise levels encountered were determined. It was hoped that such information would aid in the placement of men on jobs and that it would define the areas where ear protection was needed. After sufficient data had been obtained to make it practical, a profile system was established to systematize the noise exposures and audiometric data.

The Environmental Research Laboratory is responsible for evaluating the severity of noise exposure associated with various jobs. A General Radio sound level meter and octave band analyzer are used to determine the sound pressure levels and the frequencies of the noise to which men on a particular job are exposed. Sound pressure level determinations in octave bands are made throughout the various work areas peculiar to the job in question, and the percentage of time in each of these areas by a man doing that job is noted. The frequency, or number of times the person enters or leaves an area, is not taken into consideration; only the total percentage of time in the area is used. Each area associated with the particular job being surveyed is evaluated in a similar manner. Finally, the octave band data are combined with the duration-of-exposure data to determine the job profile for noise exposure.

#### Damage-Risk-Criteria

Basic to a profile system for evaluating noise exposures are damage-risk-to-hearing criteria. Actually chosen for use in this system were the broad-band noise levels proposed by Rosenblith and Stevens in their "Handbook of Acoustical Noise Control".<sup>1</sup> Their curve was used in the manner to be described.

#### Noise Exposure Profile System

Quiet jobs within a quiet department were profiled "A" as shown in Figure 1. This profile was used for jobs where peak noise intensities did not exceed the "negligible-risk" noise levels. No hearing conservation effort is needed for such jobs.

Quiet jobs within a noisy department were profiled "B" as indicated in Figure 2. This profile was defined as representing exposures where less than 10 per cent of the work day was spent in noise levels between the "negligible-risk" noise levels and the "damage-risk" noise levels. Hearing conservation necessary for such jobs includes a base-line audiogram record and a medical evaluation of hearing before the man is placed on the job.

Noisy jobs (Figure 3) were profiled "C". This profile was defined as representing exposures where less than 10 per cent of the work day was spent in noise that exceeds the basic "damage-risk" levels, but 10 per cent or more of the time

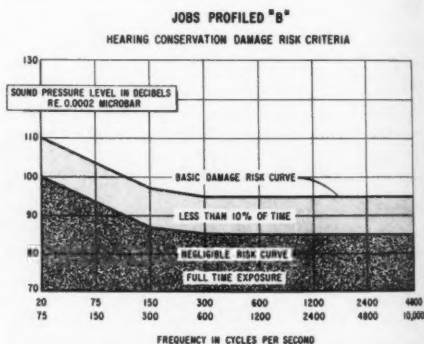


FIGURE 2. Quiet jobs within a noisy department were profiled B.

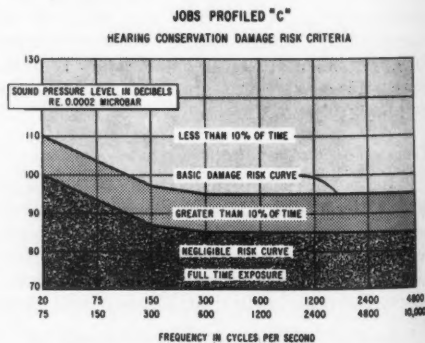


FIGURE 3. Noisy jobs were profiled C.

is spent in noise within a 10 decibel range below these levels. The hearing conservation effort necessary is a base-line audiogram and medical evaluation of hearing before a man is placed on such a job. Ear protection is "recommended" for such persons. "Recommended" ear protection means that ear plugs should be made available for use and that the men should be informed of the hazards of noise but no continuing educational program is needed. Ear plugs will be fitted at the Medical Department before the man goes to the job.

Extra noisy jobs (Figure 4) were profiled "D". These jobs represent exposures where 10 per cent or more of the work day is spent in noise that exceeds the "basic-damage-risk levels". The hearing conservation effort necessary includes a base-line audiogram and medical evaluation of hearing before job placement, periodic audiometric examinations and medical reevaluation of hearing at one year intervals, at least. Ear protection is considered "necessary". This means a continuing educational program is needed to inform the men that they may lose hearing after a period of time. Ear plugs are, of course, fitted at the Medical Department before the man goes on this job.

The second phase of the profile system is based on a medical evaluation of all employees to determine whether or not they should be placed on noisy jobs. Five profile categories have been used, ranging from a hearing classification of H-1 (acceptable for employment on a job profiled "D") to a hearing classification of H-5 (unemployable because of hearing defects). Physicians in the Medical Department have the responsibility of assigning hearing classifications to individuals and, until recently, such classifying has been done more on the basis of individual judgment than on the basis of firm facts and data. The present, rather extensive study of hearing loss as a function of noise exposure was, in part, prompted by a desire of the physicians to have something concrete upon which to base their judgments. Verifying the validity of the noise profile system was, however, the main reason for embarking on this study.

### Correlation Study

Job profiles for 294 jobs in 30 departments of The Dow Chemical Company were used as the basis for the correlation. An examination of the records showed that 2220 audiometric records had been obtained from men working on these jobs, of which 888 were repeated records dating back to 1956. To begin the job of correlating these data all audiometric records and associated

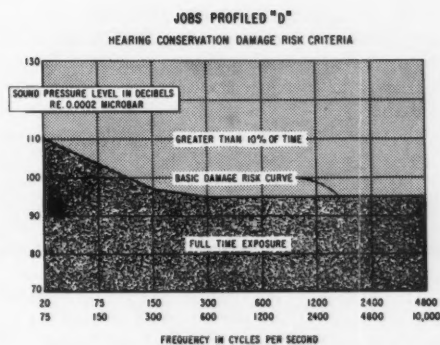


FIGURE 4. Extra noisy jobs were profiled D.

job noise exposure profile records were tabulated on I.B.M. key-punch cards. These data were then transposed onto magnetic tape for use with a Burroughs 220 computer. For this study, correlation data could best be evaluated if it were presented by the computer as composite audiograms. Therefore, the computer was programmed to calculate the average hearing loss (in decibels) and the standard deviation for each of eight test frequencies for right ears, left ears, and both ears combined as a function of nine different variables and/or the interactions of these variables. The variables chosen were the ones believed to have the most significant effects upon hearing loss.

Each of the variables considered had at least two levels. As an example, the variable "job profile", had four "levels", that is, noise exposures represented by the A, B, C and D profiles. To determine the effect of job profile (and only job profile) on hearing loss, the most recent audiograms of all men in jobs profiled "A" were averaged without regard to any other variables. Similarly, average audiograms were obtained for all men in jobs profiled B, C and D. The composite audiograms thus obtained could then be analyzed to determine whether or not noise exposures represented by the various job profiles had an effect on hearing loss. The effects of the other variables considered were determined in a similar manner.

### Variables Affecting Hearing Loss

The first variable was noise exposure intensities as represented by the job profile as previously defined. This variable was found to have a significant effect on hearing loss. That is, persons working on jobs profiled "D" were found to have much greater hearing losses than persons working on jobs profiled A, B or C.

Age was divided into four groupings, that is, 18 to 29 years, 30 to 39 years, 40 to 49 years, and 50 to 65 years. Presbycusis, or increased loss of hearing with increasing age, was evident as anticipated.

"Exposure duration" referred to the time on a job with a particular profile (that is, A, B, C or D). In this case four groupings were also used; less than 5 years, 5 to 10 years, 10 to 20 years, and greater than 20 years. We found that, as time on the job increased, so did hearing loss over and above that caused by presbycusis.

The time in years that an individual worked at a known noisy occupation prior to working at Dow was recorded, but the actual occupation was not. This variable was analyzed on a simple "yes or no" basis and individuals with pre-Dow noise exposure had more hearing loss than those without.

Military noise exposure, also, was analyzed on a "yes or no" basis, even though the number of years of such exposure was usually recorded. People with previous exposure to small arms fire, artillery or naval gun fire had a greater hearing loss than those without such exposures. Civilian gun-fire exposure such as that caused by skeet-shooting, target range shooting and extensive hunting was found to cause a significant loss of hearing in the group.

"Medical history", analyzed on a "yes or no" basis, referred to a previous history in either or both ears of ear aches, drainage, or injury; of surgery; of head injury; of ringing in the ears; of hearing loss in the immediate family; of the use of streptomycin for infection; or of scarlet fever and/or mumps. No significant difference in the hearing loss of the group with such history was found when they were compared with the group that had no "medical history".

Existing drainage from the ear canal, and

perforations or scarring of the eardrum were called "physical findings". This variable was also analyzed only on a "yes or no" basis. Those individuals with positive physical findings had a significantly increased hearing loss.

Attempts were made to determine whether or not the wearing of ear protection had an effect on hearing loss by analyzing the data on the basis of whether ear protection was worn always, frequently, seldom or never. Unfortunately, most of the men were found to have worn ear protection seldom or never, and therefore no conclusions could be drawn.

After a preliminary examination of all nine variables, attention was fixed on the first three; namely, job profile, age, and exposure duration. In order to refine the available data as much as possible so that only the effects caused by the action of those three variables would be considered, elimination of the effects of other causes of hearing loss was necessary. Therefore, the data were put through "sieves" (by the computer) which eliminated from further consideration men who had pre-Dow industrial noise exposure, military noise exposure, civilian-gun fire exposure and those men showing positive evidence of ear defects. After thus screening the data there remained a group of 651 individuals whose audiograms were of interest.

### Effects of Age

Composite audiograms for the selected group were determined as a function of the four job profile categories, the four age groupings, and the four duration-of-exposure groups. For each job profile a composite audiogram could be plotted for each of the age groups, or for each of the exposure-duration groups. For every point on each of these composite audiograms the average age and the average years of exposure were determined. Although the data indicated that the average hearing loss for left ears was slightly greater (less than four decibels) than for right ears, the difference was considered not great enough to prevent the use of "combined ears" data for comparison purposes.

As previously indicated, job profile "A" refers to a quiet job within a quiet department and, therefore, men in this category have had no significant noise exposure. By determining their composite audiogram as a function of age (Figure 5) the data may be compared with published presbycusis curves.

The presbycusis curves shown in Figure 6 were reported by Kryter and Beranek in their recent book "Noise Reduction"<sup>12</sup> and consist of data as weighted averages from five separate

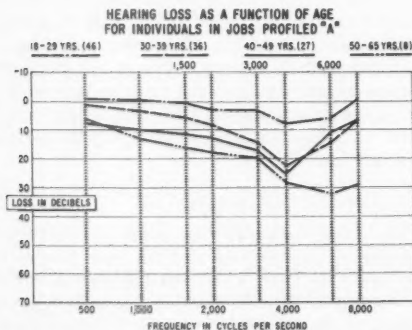


FIGURE 5. Hearing loss as a function of age for men in jobs profiled A.

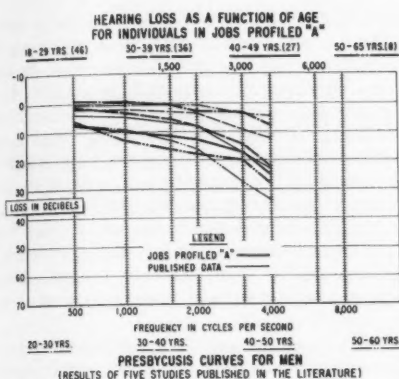


FIGURE 6. Comparison of hearing loss of men in jobs profiled A with published presbycusis data.

hearing surveys. Their data was then, based upon a rather large group of people while data from this survey was based on audiograms from 118 men. Considering the discrepancy in numbers, excellent agreement was shown.

#### Effects of Exposure Duration

An examination of hearing loss for the 118 individuals working in jobs profiled "A" as a function of exposure duration (Figure 7) shows that hearing loss follows the pattern of presbycusis. This is not at all surprising as duration of exposure is certainly correlated rather closely with age. After these data had been corrected for presbycusis (Figure 8) duration of exposure alone was noted to have caused no significant change in hearing. There appears to be no practical significance which can be attached to the 5 decibel loss shown in the lower frequencies for individuals with 25 year's exposure because this loss was not repeated for the group of men working in jobs profiled "B."

The uncorrected hearing loss for the 268 men in jobs profiled "B," shown by Figure 9, again showed a pattern very similar to the loss expected with normal ageing. These data, however, appeared to indicate that those men with less than 10 years noise exposure experienced the greatest loss in the higher frequencies. However, when the data were corrected for presbycusis (Figure 10), the hearing loss for these individuals was essentially no greater than the hearing loss for men working on jobs profiled "A."

In fact, the hearing loss that can be expected after 25 years exposure for men working in jobs profiled either "A" or "B" is less than 8 decibels. This evidence lends considerable support to the

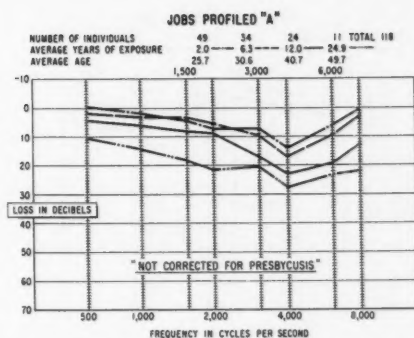


FIGURE 7. Hearing loss as a function of exposure duration for men in jobs profiled A, not corrected for presbycusis.

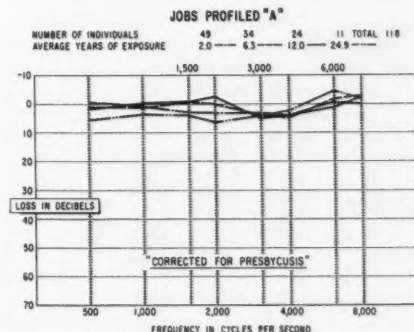


FIGURE 8. Hearing loss as a function of exposure duration for men in jobs profiled A, corrected for presbycusis.

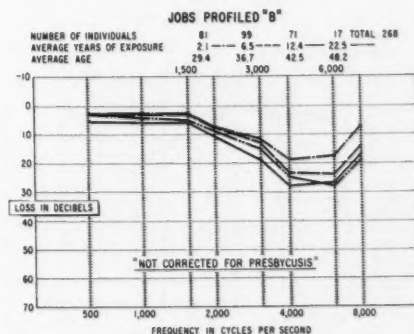


FIGURE 9. Hearing loss as a function of exposure duration for men in jobs profiled B, not corrected for presbycusis.



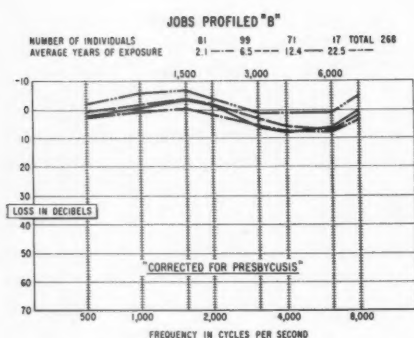


FIGURE 10. Hearing loss as a function of exposure duration for men in jobs profiled B, corrected for presbycusis.

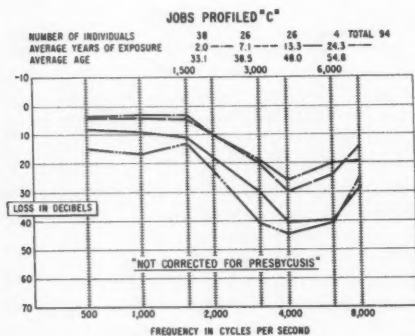


FIGURE 11. Hearing loss as a function of exposure duration for men in jobs profiled C, not corrected for presbycusis.

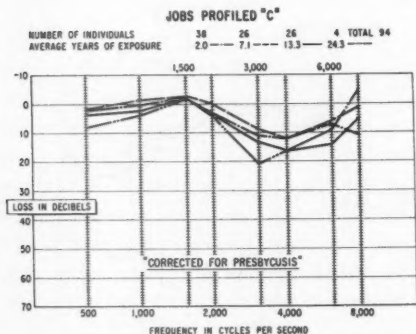


FIGURE 12. Hearing loss as a function of exposure duration for men in jobs profiled C, corrected for presbycusis.

basic damage risk criteria which has been used. It can be said with a good deal of certainty that when a man has no exposure exceeding the basic "damage-risk" level, and spends less than 10 per cent of his work day in noise exceeding the "negligible-risk" level he can work at least 25 years without experiencing any more hearing loss than would be expected with normal ageing.

The 94 men working in jobs profiled "C" (Figure 11) showed a definitely greater hearing loss at the higher frequencies than did men working in jobs profiled "A" or "B." This loss of hearing is evident with less than 5 years of noise exposure.

The data corrected for presbycusis (Figure 12) showed a consistent wide dip in the higher frequencies for all exposure durations. There appeared to be little difference between the curves for exposures of 2 and 7 years, but the loss at 13 years appeared to be somewhat greater. The curve for 24 years' exposure is rather erratic, probably because it represents data from only four individuals while the other curves were based on data from twenty-six to thirty-eight men.

The general conclusions to be drawn from this particular group appear to be first, that most of the hearing loss is experienced in the first 5 or so years of exposure, second that the hearing loss for individuals working in jobs profiled "C" does not increase proportionately with exposure duration and finally, that even 24 years on the job does not result in a major loss of hearing. Ear protection should certainly be encouraged for men starting jobs profiled "C," but such protection may or may not be beneficial for men who have been working at such jobs for several years.

The composite audiograms as shown in Figure 13 represent data from 171 men working in jobs

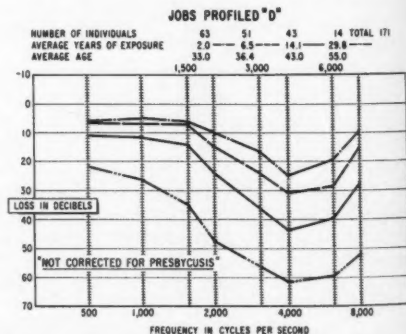


FIGURE 13. Hearing loss as a function of exposure duration for men in jobs profiled D, not corrected for presbycusis.

profiled "D." There appears to be no doubt that hearing loss is progressive with increasing exposure duration. There is considerably more spread between the various curves than on the previous audiograms, and hearing at low as well as at high frequencies is affected.

These data, corrected for presbycusis (Figure 14) show that the loss of hearing with increased exposure duration was nearly uniform at all frequencies. A close look at the data showed that at the test frequencies of 2000, 3000 and 4000 cycles per second the loss of hearing was about 1 decibel per year of exposure. This evidence provides further confirmation of the damage risk criteria used. Loss of hearing will most certainly be the result when a man spends more than 10 per cent of his work day in noise levels exceeding the damage-risk curve. Ear protection is "necessary" to prevent loss of hearing.

#### Susceptibility to Noise

Our data, unfortunately, do not show definitely whether or not young ears are more susceptible to noise-induced hearing loss than older ears. In examining the composite audiograms for individuals working in jobs profiled "C" it appears that a significant loss of hearing had developed at an average of 2 years noise exposure (for individuals whose average age is 33), and that therefore, young men may be more sensitive to noise than older men. However, the data for individuals in jobs profiled "D" indicated that hearing loss is a linear function of time on the job, and that men with two years on these jobs had about the same loss as men with two years on jobs profiled "C." In addition, the older men in jobs profiled "D" (that is, those who had been on the job longest) showed a much greater loss in hearing than those men with similar ages in jobs profiled "C." These data are obviously not sufficient to completely resolve the problem of age versus susceptibility to acoustic trauma.

#### Summary

To return to the questions that were to be answered with this correlation study; first, does working on a noisy job cause significant impairment of hearing? The answer is definitely yes. Men working on jobs which have been profiled "C" and "D" show hearing losses greater than those expected with ageing. Men who already have a significant hearing loss should, therefore, not be assigned to jobs profiled "D."

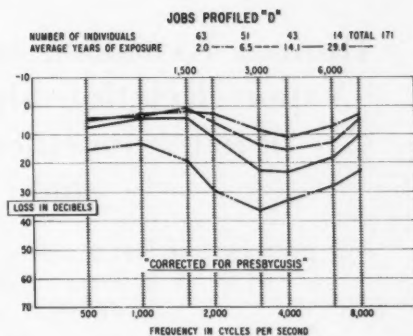


FIGURE 14. Hearing loss as a function of exposure duration for men in jobs profiled D, corrected for presbycusis.

The next question was whether or not there is a definite need for men working on noisy jobs to wear ear protection in order to prevent loss of hearing. The answer is again "yes". Men working on jobs profiled "D" definitely need to wear ear protection and men, especially those with good hearing, entering jobs profiled "C" should be encouraged to wear ear protection.

Finally, is there justification for moving men with significant hearing loss to quieter jobs regardless of their age? The data certainly indicate that a loss of hearing does not protect against further loss, especially for men working on the extra noisy jobs profiled "D." The answer to the question, then, would appear to be definitely "yes" if only "D" jobs are considered. However, there does not appear to be sufficient justification to move men from jobs profiled "C" regardless of age. Instead, men working on such jobs should have ear protection made available to them and they should be encouraged to wear it.

#### Acknowledgment

The authors express their appreciation to Mr. J. L. Williams of the Computations Research Laboratory for his assistance in this study.

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# Human Exposure to 1,1,1-Trichloroethane Vapor: Relationship of Expired Air and Blood Concentrations to Exposure and Toxicity

RICHARD D. STEWART\*, M.D., HAROLD H. GAY, M.D.,  
DUNCAN S. ERLEY, M.S., CARL L. HAKE, Ph.D.,  
and ARNOLD W. SCHAFFER, B.S.

*Medical Department, Chemical Physics Research Laboratory, and Biochemical Laboratory,  
The Dow Chemical Company, Midland, Michigan*

A study of controlled human exposures to 1,1,1-trichloroethane vapor has revealed a prolonged exponential "decay curve" when the concentration in the postexposure expired air is plotted against hours after exposure. This measurement was predictable enough to allow a reasonable estimation of the magnitude of exposure. Chemical, physiological, and clinical laboratory studies were carried out and correlated with the vapor exposures. The determination of urinary urobilinogen proved to be the most sensitive test of liver stress produced by markedly excessive exposures to 1,1,1-trichloroethane. Data from this study support 500 ppm as a satisfactory threshold limit for this compound.

## Introduction

THE probability of human exposure to the vapors of 1,1,1-trichloroethane is increasing rapidly as this compound gains popularity as a solvent in cold degreasing applications. Because of its low toxicity, its use as a solvent in several other applications, *e.g.*, agricultural chemicals, hair sprays, and dry cleaning, is also being investigated. Thus, the physician, the industrial hygienist, and the toxicologist will be called upon to evaluate acute and chronic exposures to 1,1,1-trichloroethane vapor in an increasingly large segment of the population.

A major obstacle which has prevented accurate evaluation of the significance of exposures to 1,1,1-trichloroethane vapor has been the lack of a practical method to identify and measure the concentration of the compound in the blood or expired air of the exposed individual. This has prevented a correlation of the blood or expired air concentration with the magnitude of exposure. A second obstacle has been the lack of a reliable means of determining the magnitude of an accidental exposure after it has occurred.

It is the purpose of this paper to report a series of acute human exposures to 1,1,1-trichloroethane vapor in which these obstacles were studied. Volunteers were exposed in a chamber in which the concentration of 1,1,1-trichloroethane vapor was controlled by simultaneous atmospheric analyses. Concentration of the chemical in the blood was determined by infrared spectrometric methods described previously,<sup>1,2</sup> while postexposure expired air concentration was determined directly through the use of an infrared spectrometer employing a long path-length gas cell. Blood and expired air concentrations were then correlated with the magnitude of the exposure and with the physiological effects of the 1,1,1-trichloroethane.

## Experimental Procedure

A series of timed human exposures to known concentrations of 1,1,1-trichloroethane vapor was conducted. The first two exposures to be described, Experiments 1 and 2, were to atmospheric concentrations of 500 ppm. During the next exposure, which was to an atmospheric concentration approaching 1000 ppm, subjects were removed from the exposure chamber at three time-intervals. These groups will be discussed as Experiments 3, 4, and 5. The above concentrations were chosen because of the studies

Presented at the Twenty-second Annual Meeting of the American Industrial Hygiene Association, Detroit, Michigan, April, 1961.

\* Present address: Department of Internal Medicine, University of Michigan Medical Center, Ann Arbor, Michigan.

of Torkelson, *et al.*,<sup>3</sup> which indicated that the atmospheric concentration of 1,1,1-trichloroethane for daily exposures of 7 to 8 hours duration should not exceed 500 ppm, and that concentrations approaching 1000 ppm would have anesthetic effects. In a final exposure, Experiment 6, the atmospheric concentration was increased rapidly until anesthetic levels were reached. Table I outlines the time and degree of exposure for the experiments in this series.

#### Material Used

The 1,1,1-trichloroethane ( $\text{CH}_3\text{CCl}_3$ ) used in this series of experiments was the inhibited product, commercially available Chlorothene<sup>4</sup> solvent. Chlorothene solvent has the following composition: 94 to 97% 1,1,1-trichloroethane, 2.4 to 3.0% dioxane, 0.12 to 0.3% butanol, and small amounts of ethylene dichloride, water and other materials. The acute toxicity and the vapor pressure of Chlorothene have been shown to be essentially identical with those of 1,1,1-trichloroethane.<sup>3</sup> The latter designation will generally be used throughout this paper since infrared analysis specifically identifies this chemical in the composition.

#### Exposure Chamber

An interior room, measuring 11'  $\times$  12'  $\times$  7'2" high, served as the exposure chamber. The room had a continuous positive air supply. After the subjects were seated in the closed room, Chlorothene was poured into a flat, partially covered dish. A pedestal fan was used to blow air across the dish and circulate the vapors throughout the room. As seen in Table I, it was possible to keep the atmospheric concentration of the 1,1,1-trichloroethane within the room relatively constant by regulating the exposed surface area of the material in the dish.

#### Analysis of Exposure Atmosphere

The atmospheric concentration of 1,1,1-trichloroethane in Experiment 6 was determined by absorption of known volumes of air on silica gel.<sup>5</sup> In the exposure to atmospheric concentrations just over 900 ppm, three monitoring methods were simultaneously employed; two Dow-modified Davis Halide Meters,<sup>6</sup> a Perkin-Elmer Model 12C<sup>7</sup> infrared spectrometer equipped with a 10-meter path-length gas cell, and a Draeger Gas Detector Kit.<sup>8</sup> At the lowest level of exposure, 500 ppm, one Dow-modified Davis Halide meter was used to monitor the atmosphere in Experiment 2, while in Experiment 1 both the Halide Meter and the infrared spectrometer were used.

TABLE I  
Human Exposure to 1,1,1-Trichloroethane Vapor

Experiment	No. of Subjects	Desired Concentration (ppm)	Time to Reach Desired Conc. (min)	Length of Total Exposure (min)	Concentration <sup>a</sup> During Total Exposure (ppm)	Range After Reaching Desired Concentration (ppm)
1	6	500	13	78	500 (average of methods) 470 (Davis Halide) 531 (Infrared)	305-575 301-655
2	6	500	8	186	496 (Davis Halide)	420-610
3	3	1000	5	73	955 (average of methods) 978 (Davis Halide #1) 961 (Davis Halide #2) 931 (Infrared) 950 (Draeger)	855-1075 710-1090 750-1075
4	2	1000	5	35	910 (average of methods)	Same as Exp. 3
5	3	1000	5	20	900 (average of methods)	Same as Exp. 3
6	7	anesthetic	15	15	1380 (silica gel)	0-2650 <sup>b</sup>

<sup>a</sup> Time-weighted average concentrations.

<sup>b</sup> Range from start to finish.

With the exception of the Draeger Detector Kit which was used in the chamber, air from the chamber was sampled by the use of probes of saran tubing suspended to head height at the center of the room. These probes were passed under the door to the continuous monitoring devices outside. The Halide Meter and the infrared spectrometer were coupled to recorders which provided a continuous record of the concentration. These machines were calibrated against known concentrations of 1,1,1-trichloroethane. At the higher concentration of 1,1,1-trichloroethane, the blue glass filter of the Halide Meter required frequent cleaning, therefore two meters were used. As seen in Table I, Experiment 3, the data obtained from each of the three monitoring techniques showed remarkably close agreement. The time-weighted average from each method was therefore used, when more than one monitoring device was

used, to calculate an overall average for the respective experiment.

### Subjects

Healthy male volunteers from The Dow Chemical Company, ranging in age from 30 to 60 years were selected for the exposure studies. Each subject had received a complete pre-employment history and physical examination, chest x-ray and, in some cases, lumbar spine x-ray, complete blood count (C.B.C.), urinalysis, and orthorator eye examination. Each subject had then been followed by the Medical Department with periodic history and physical examinations, which included chest x-ray, C.B.C., urinalysis, orthorater check, and, in recent years, timed vital capacity and audiometric examination. Only one subject had an abnormal physical finding. The 60-year old male had a liver palpable 4 cm below the right costal margin, but there was no history of liver disease, and liver function tests were within the normal range.

Several of the same subjects participated in all of these exposures. No subject participated in any exposure who had had a known exposure to any chlorinated hydrocarbon within the previous six days.

### Preexposure and Postexposure Data

Immediately before each exposure the following clinical data and laboratory samples were obtained from each subject: blood pressure, expirogram (timed vital capacity), serum for glutamic oxaloacetic transaminase (SGO-T) and urine for urinary urobilinogen. Preexposure blood, urine and expired air samples were analyzed for 1,1,1-trichloroethane for control purposes. A complete urinalysis was obtained both before and after several of the exposures. A 15-minute phenolsulfonphthalein (P.S.P) determination was done before and after Experiment 2. Table II lists the pre- and postexposure data obtained.

During the exposures serial urine and blood samples were obtained for analysis of 1,1,1-trichloroethane. Subjective responses were noted. Romberg and heel-to-toe tests were performed at 15-minute intervals by those in Experiments 1, 3, 4 and 5.

Following the exposures, serial samples of blood, urine, and expired air were analyzed for 1,1,1-trichloroethane. Preexposure laboratory tests were repeated at appropriate intervals (see Table II). Expirograms and blood pressures were obtained within 5 to 10 minutes following the exposures in which these were studied.

### Analysis of Blood, Urine, and Expired Air for 1,1,1-Trichloroethane

Venous blood was obtained through an indwelling siliconized 20-gauge needle equipped with a siliconized stylet. Two ml of blood were added to a 4-ml aluminum-capped, glass vial containing 2 ml of carbon bisulfide and one drop of 0.83% heparin solution. The sample was gently agitated by end-over-end inversion for 5 minutes. The solvent was withdrawn and analyzed for 1,1,1-trichloroethane in a double beam infrared spectrometer.<sup>7,9</sup> This method for determining organic compounds in biological fluids has been described previously in detail.<sup>1,2</sup> Voided urine samples were analyzed in a similar manner. The minimal amount of the compound detectable in blood and urine by this solvent extraction technique was 1 ppm with an accuracy of  $\pm 1$  ppm.

Expired air samples were collected in six-liter volume saran bags. The bagged air was allowed to flow into the evacuated ten-meter path-length gas cell, and was scanned on the appropriate spectrometer. The absorbance at  $9.2\mu$  was measured to determine the concentration of 1,1,1-trichloroethane. The minimal amount of the compound detectable in expired air was 0.5 ppm with an accuracy of  $\pm 0.1$  ppm.

### Results

#### Experiment 1, 500 ppm, 78 minutes

Six subjects were exposed to 1,1,1-trichloroethane at 500 ppm (the Threshold Limit recommended by the American Conference of Governmental Industrial Hygienists) for 78 minutes. From a subjective standpoint, no significant untoward effects were noted. Three of six subjects noted a slight eye irritation which rapidly disappeared. There was no dizziness noted; balance and coordination were unaffected. Pre- and postexposure clinical laboratory data, listed previously, were normal with the exception of subject 5 who exhibited a trace of albumin and 3-6 red blood cells per high power field (RBC/HPF) in the 20-hour postexposure urine. The relationship of this observation to the exposure was questionable.

Analysis of serial blood samples obtained during the exposure revealed that the average concentrations of 1,1,1-trichloroethane in the blood at 30, 60 and 75 minutes after the start of the exposure were all between 3 and 4 ppm, with a range of 1.5 to 6.5 ppm. Twenty-five minutes after cessation of exposure, the compound was just detectable in the blood of 4 of the 6



TABLE II  
1,1,1-Trichloroethane Pre- and Postexposure Data

	Sub- ject	SGO-T			Urinary Urobilinogen				Urinalysis				15 min. P.S.P.	
		Preexposure	20 hr. Post	7 da. Post	Preexposure	6 hr. Post	20 hr. Post	7 da. Post	Preexposure		20 hr. Postexposure		Preex- posure	20 hr. Post- exposure
									Alb.	Micro.	Alb.	Micro		
Normal Value		6-40			1:40 or less				0-5 RBC/HPF				Greater than 25%	
Experiment 1 500 ppm, 78 min.	1	22	10	12	1:10		1:10	1:10	neg	neg	neg	neg		
	4	14	14	10	1:10		1:10	1:10	neg	neg	neg	rare RBC		
	5	15	9	16	1:10		1:10	1:10	neg	rare RBC	trace	3-6 RBC		
	6	16	10	12	1:10		1:10	1:10	neg	1-2 RBC	neg	rare RBC		
	8	16	16	14	1:10		1:10	1:10	neg	rare RBC	neg	rare RBC		
	11	12	16	14	1:10		1:10	1:10	neg	neg	neg	neg		
Experiment 2 496 ppm, 186 min.	1	20	20	14	1:10		1:10	1:10					39%	44%
	2	20	18	16	1:10		1:10	1:10					38%	31.5%
	5	16	16	10	1:10		1:10	1:10					40%	39%
	6	23	20	18	1:10		1:10	1:10					43%	44%
	8	20	18	19	1:10		1:10	1:10					29%	24%
	10	24	19		1:10		1:10	1:10						
Experiment 3 955 ppm, 73 min.	5	16	18	16	1:10		1:10	1:10	neg	0-2 RBC	neg	rare RBC		
	6	19	16	12	1:10		1:10	1:10	neg	neg	neg	neg		
	8	18	16	15	1:10		1:10	1:10	neg	neg	neg	neg		
Experiment 4 910 ppm, 35 min.	3	14	16	6	1:10		1:10	1:10	neg	rare RBC	neg	rare RBC		
	4	18	18	16	1:10		1:10	1:10	neg	neg	neg	neg		
Experiment 5 900 ppm, 20 min.	2	17	15	14	1:10		1:10	1:10	neg	rare RBC	neg	neg		
	7	18	20	17	1:10		1:10	1:10	neg	neg	neg	neg		
	9	16	18	20	1:10		1:10	1:10	neg	neg	neg	neg		
Experiment 6 0-2650 ppm, 15 min.	1	14	16	15	1:10	1:640	1:10	1:40	neg	neg	neg	neg		
	2	16	15	15	1:10		1:10	1:10	neg	neg	neg	neg		
	3	10	11	16	1:10	1:640	1:10	1:10	neg	neg	neg	rare RBC		
	4	14	14	18	1:10	1:10	1:10	1:10	neg	neg	neg	rare RBC		
	5	14		14	1:10		1:10	1:10	neg	neg	neg	neg		
	6	15	15	19	1:10		1:10	1:10	neg	neg	neg	0-2 RBC		
	7	14	16	20	1:10	1:40	1:10	1:20	neg	neg	neg	1-5 RBC		

subjects. Urine samples taken during exposure indicated that some samples possibly contained up to 2 ppm 1,1,1-trichloroethane, while none was detected in one sample. The samples obtained 15 minutes after exposure revealed the presence of a trace amount of 1,1,1-trichloroethane in 2 of the 6 samples, while none was detected in the other four.

The expired air concentrations of 1,1,1-trichloroethane, plotted versus time obtained following the exposure, are graphed on log-log paper in Figure 1. A free-hand curve was drawn through points representing the average expired air concentrations. Each point, with its maximum and minimum, represents the average of all of the available samples at that given time postexposure. The number of samples was never less than 4, and was usually 6. Points plotted without maximum and minimum designations

represent individual samples. Concentrations at 24 hours postexposure were near the lower limit of sensitivity, 0.5 ppm.

#### Experiment 2, 496 ppm, 186 minutes

Six subjects were exposed to the Threshold Limit recommended for 1,1,1-trichloroethane for approximately 3 hours (186 minutes). From a subjective standpoint, no untoward effects were noted. No eye irritation or dizziness occurred. Balance and coordination were unaffected. Pre- and postexposure clinical data, listed in Table II, were normal.

Analyses for 1,1,1-trichloroethane in the blood and urine during and following exposure were inaccurate because the samples were processed in the exposure chamber, allowing contamination of the carbon disulfide used for extraction. In all other experiments, transfer of the

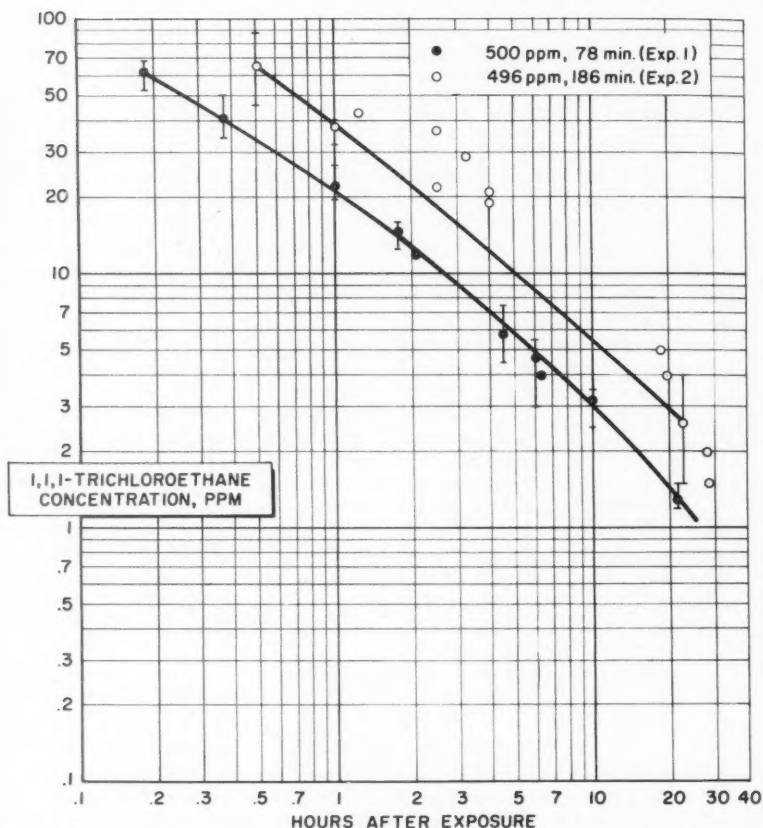


FIGURE 1. 1,1,1-Trichloroethane Expired Air Concentration. Humans were exposed to atmospheric concentrations of 500 ppm for 78 minutes (Exp. 1) and 496 ppm for 186 minutes (Exp. 2).

extractant was done outside the exposure chamber.

The average concentrations of 1,1,1-trichloroethane in the expired air following exposure are also plotted in graph form in Figure 1. Due to leakage from unsealed bags, many samples did not contain sufficient air for analysis after holding overnight. Therefore there were only three times at which five or more samples obtained simultaneously could be analyzed. The averages of these are designated with a maximum and minimum. Individual values are denoted without a maximum and minimum. A free-hand curve was drawn between the points representing average values.

*Experiments 3, 4 and 5; 900 to 955 ppm for 73, 35 and 20 minutes*

Three subjects were exposed to 955 ppm of 1,1,1-trichloroethane vapor for 73 minutes, two

subjects to 910 ppm for 35 minutes and three subjects to 900 ppm for 20 minutes. The subjective and physiological responses are recorded in Table III. Within three minutes following the conclusion of the exposures no subject experienced any difficulty in performing a normal Romberg test. No difficulty in performing simple mental calculations was experienced, neither were there any untoward effects such as malaise, headache, or nausea noted following these exposures.

The concentrations of 1,1,1-trichloroethane in the blood during the exposure to 955 ppm for 73 minutes were as follows: 1 ppm at 15 minutes, 2-4 ppm at 30 minutes, and 7-10 ppm at 65 minutes after the start of the exposure. None of the chemical could be detected in the blood samples taken 30 minutes after the end of the exposure. In the groups exposed to 910 ppm and

900 ppm, in which exposures were of shorter duration, a similar rise in blood concentration was noted while the subjects were in the exposure chamber. The concentration of 1,1,1-trichloroethane in the urine at 45 minutes after the start of the exposure was 1-2 ppm in Experiment 3. Samples obtained seven minutes following exposure did not contain the compound in detectable amounts. In the shorter experiments the compound was not detected in the urine either during the exposure to postexposure.

Pre- and postexposure clinical laboratory data obtained from the three groups are listed in Table II. One subject who had a 20-minute exposure to an average concentration of 900 ppm had an elevated urinary urobilinogen 7 days after exposure. The remainder of the clinical laboratory data was normal. There also was no change in the timed vital capacity or blood pressure values.

Average concentrations of 1,1,1-trichloroethane in the expired air following these exposures are plotted versus hours after exposure in Figure 2. Each point with its maximum and minimum, plotted for Experiments 3 and 5 represents the average of 3 values. The upper two points of those plotted for Experiment 4 each represent the average of 2 values and the others a single value.

#### Experiment 6, 0 to 2650 ppm, 15 minutes

Seven subjects were exposed to a constantly increasing atmospheric concentration of 1,1,1-trichloroethane. When two of the subjects no longer were able to stand, the experiment was halted. This occurred at a peak vapor concentration of 2650 ppm. The total time of exposure was 15 minutes.

The subjective and physiological responses observed during this exposure are recorded in Table IV. Within the first five minute interval following the exposure all subjects had fully regained their sense of equilibrium. No nausea or vomiting occurred. It required marked concentration during the first fifteen minutes following exposure to perform simple mental calculations accurately. The five subjects who had become lightheaded stated that they didn't "feel normal" until approximately three hours following the exposure. They defined this abnormal feeling as "malaise."

The concentration of 1,1,1-trichloroethane in the blood 9 minutes following exposure was  $5 \pm 1$  ppm, while 20 minutes following exposure the compound was questionably detectable in blood (0.5-1 ppm). Urine, collected 15 minutes following exposure, did not contain measurable amounts of 1,1,1-trichloroethane.

TABLE III  
Subjective and Physiological Responses to  
1,1,1-Trichloroethane Vapor Concentrations  
of 900 to 1000 ppm

Average Concentration	Responses to Exposure*
900 ppm for 20 minutes (3 subjects) (Exp. 5)	Positive Romberg in 1 subject. Greater effort required to perform a normal Romberg in 2 subjects after 10 minutes of exposure. Heel-to-toe walking normal. Two subjects experienced lightheadedness above 900 ppm.
910 ppm for 35 minutes (2 subjects) (Exp. 4)	Greater mental effort required to perform a normal Romberg test after 10 minutes of exposure. All heel-to-toe walking performed well. One subject experienced persistent lightheadedness above 900 ppm.
951 ppm for 73 minutes (3 subjects) (Exp. 3)	Greater mental effort required to perform a normal Romberg test after 10 minutes of exposure. After 15 minutes of exposure one subject had consistently positive Romberg. Heel-to-toe walking performed well by all during exposure. No lightheadedness.

\* Mild eye irritation was noted by all subjects when vapor concentrations rose above 1000 ppm.

Pre- and postexposure clinical laboratory data are listed in Table II. Two laboratory findings of questionable significance were noted following the exposure. Two subjects had positive urinary urobilinogen 1:640, noted to be present seven hours postexposure. A repeat urobilinogen test twenty hours postexposure was negative for all subjects. Five subjects were noted to have from 1 to 2 RBC/HPF on a centrifuged urine sample, obtained sixty minutes postexposure, whereas no red blood cells had been detected prior to exposure. It is to be remembered that dioxane (the inhibitor) in sufficient concentration is a renal toxin. No change occurred in the timed vital capacities or blood pressure measurements.

The mean and the range of the expired air concentrations of 1,1,1-trichloroethane following exposure are graphed on log-log paper in Figure 3.

#### Discussion

It was noted after the first exposure to 1,1,1-trichloroethane at its Threshold Limit that this compound was detectable in the expired air for many hours after exposure. From the work of Hake, *et al.*,<sup>10</sup> it was known that the rat expires unchanged almost all of an intraperitoneal dose of 1,1,1-trichloroethane- $C^{14}$ . Therefore it was not surprising that the compound could be detected in human expired air after an exposure. However, it was not predictable that it would be

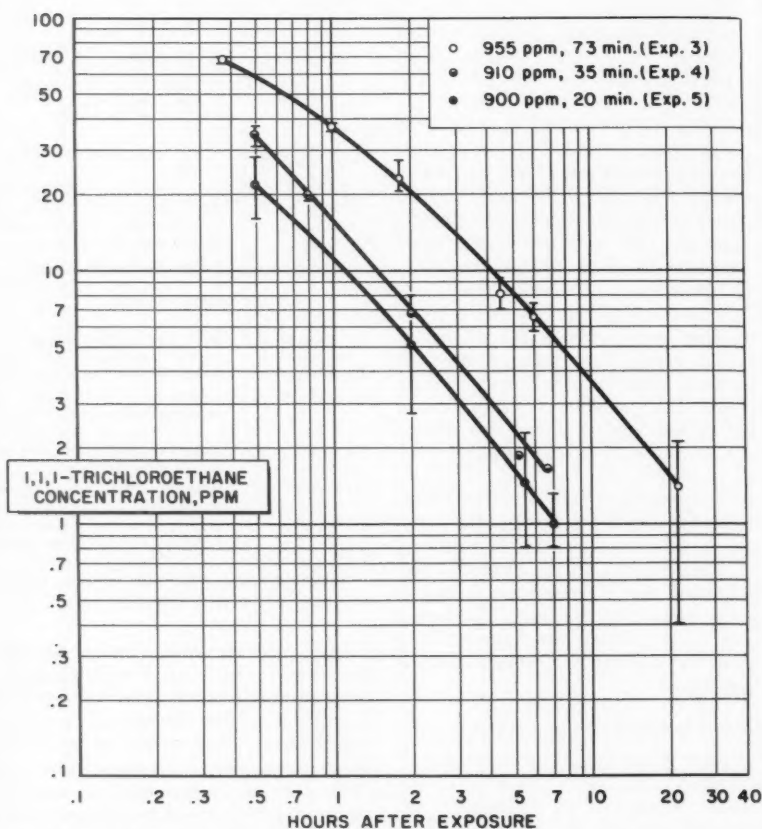


FIGURE 2. 1,1,1-Trichloroethane Expired Air Concentration. Humans were exposed to atmospheric concentrations of 955 ppm for 73 minutes (Exp. 3), 910 ppm for 35 minutes (Exp. 4), and 900 ppm for 20 minutes (Exp. 5).

detected more than 20 hours after an exposure to approximately 500 ppm, the recommended Threshold Limit. When this long expiration time was found, it suggested that the measurement of the compound in the postexposure expired air might be helpful in estimating the magnitude of the exposure.

It was found that the most significant manner in which the concentration of 1,1,1-trichloroethane in the expired air could be compared to the time after exposure (decay curve) was by plotting these points on log-log graph paper. From the plot of these points in Figure 1, it can be seen that the decay curve is almost a straight line and it can therefore be concluded that the expiration of 1,1,1-trichloroethane has an inverse exponential relationship to time after exposure. Figure 1 also demonstrates another important point. From a comparison of the two

decay curves after 78- and 186-minute exposures to 500 ppm, it can be seen that the duration of exposure has a direct bearing on the concentration of 1,1,1-trichloroethane in the expired air, especially during the early hours after exposure.

It was of interest to further determine the effect of the length of exposure on the expired air decay curve. Figure 2, in which the decay curves for 20-, 35-, and 73-minute exposures to 1,1,1-trichloroethane concentrations of just over 900 ppm are plotted, shows that though the two curves from the 20- and 35-minute exposures contain considerable overlap, the 73-minute exposure gives a much higher curve. This would also indicate that the decay curves are sensitive to length of exposure differentials at higher exposure concentrations.

Figure 4 demonstrates the effect of exposure

TABLE IV

Subjective and Physiological Responses to a Constantly Increasing 1,1,1-Trichloroethane Vapor Concentration Over a Period of Fifteen Minutes

Concentration (ppm)	Responses to Exposure
0-1000	Increasing awareness of a slightly sweet, not unpleasant odor.
1000-1100	Mild eye irritation noted in 6 of 7 subjects.
1900-2000	6 of 7 subjects aware of throat irritation.
2600	1 subject very lightheaded.
2650	2 subjects unable to stand. 3 subjects very lightheaded, but able to stand. 2 subjects were not lightheaded, and one of these was able to demonstrate a normal Romberg test.

concentration upon the decay curve when the time of exposure is held constant. Points from Experiments 1 and 3 are plotted for comparison. It can be seen that for the first 2 to 3 hours after exposure there was no overlapping of points from the exposures to 500 and 955 ppm of equal duration. More than 4 hours after exposure, there was some overlapping of points, with the probability becoming greater as time after exposure increased. From this limited data, it appears that a valid conclusion as to the atmospheric exposure concentration of 1,1,1-trichloroethane can be drawn from the decay curve after an exposure if the duration of exposure is known. Many more experiments of differing duration and concentrations would have to be carried out in order to determine a family of curves. However, from the data in this paper, one could conclude with reasonable accuracy whether a person had been exposed to 500 or 900 ppm, if the dura-

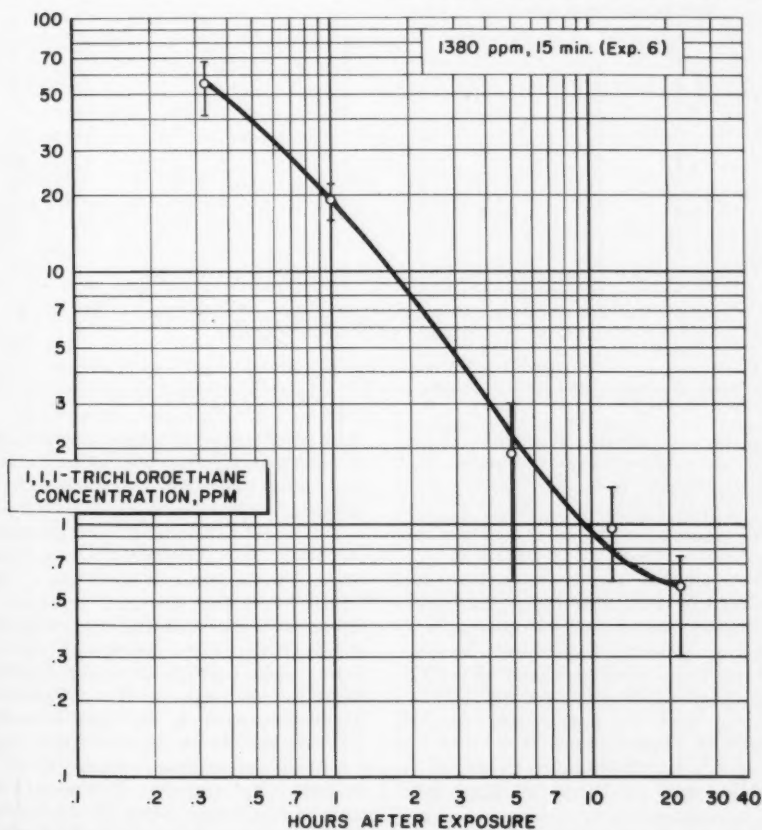


FIGURE 3. 1,1,1-Trichloroethane Expired Air Concentration. Humans were exposed to a rising concentration, 0 to 2650 ppm, of 1,1,1-trichloroethane for 15 minutes (Exp. 6).



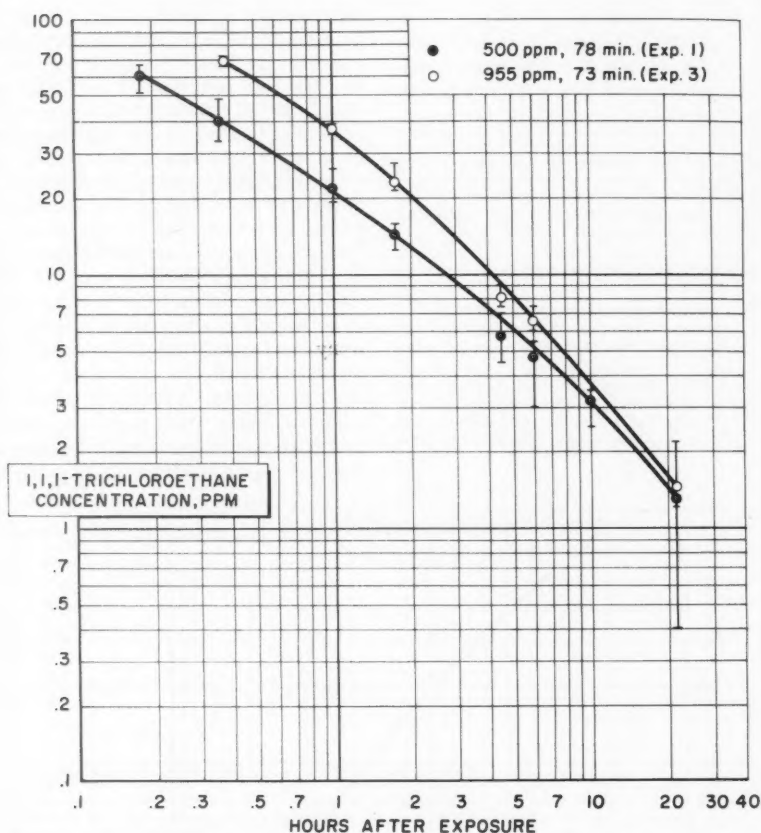


FIGURE 4. 1,1,1-Trichloroethane Expired Air Concentration. Comparison of exposures of nearly equal length; 500 ppm for 78 minutes (Exp. 1) and 955 ppm for 73 minutes (Exp. 3).

tion of exposure was about 70 minutes. It may be possible to obtain a family of curves which would be applicable to human exposures by exposing animals for various periods of time to several concentrations of 1,1,1-trichloroethane.

Infrared analysis of the postexposure expired air for measuring 1,1,1-trichloroethane proved to be an efficient method for three reasons. First, it provided an absolute, quantitative identification of 1,1,1-trichloroethane vapor. Second, it was rapid. One minute was required to obtain the air sample while five minutes were required for the analysis. Third, it was sensitive to  $0.5 \pm 0.1$  ppm of 1,1,1-trichloroethane in air, allowing the detection of the compound many hours after the exposure occurred.

This infrared method has proven useful for the

analysis of other chlorinated hydrocarbons in the expired air,<sup>11, 12</sup> as well as for other volatile compounds possessing strong absorption in the infrared.<sup>13</sup>

The concentration of 1,1,1-trichloroethane in the blood was determined by measuring the change in the infrared spectrum at the wave length where this chemical is known to have strong absorption. Though the results obtained indicated a positive relationship between the concentration of 1,1,1-trichloroethane in the blood and the concentration in the atmosphere, the concentrations in the blood were at such a low level that the results were not of significance for predicting exposure concentrations, neither were they high enough to give an infrared spectrum which could positively be identified as that of 1,1,1-trichloroethane. From the results

of the exposure to near anesthetic concentrations, it would appear that the blood of a person overcome by 1,1,1-trichloroethane vapor would probably attain the 10-15 ppm concentration necessary for a positive identification of 1,1,1-trichloroethane by its infrared spectrum. The results of the urine analyses verify the experiments of Hake, *et al.*<sup>10</sup> in which it was found that only trace amounts of 1,1,1-trichloroethane are excreted in the urine. Urinary analysis for 1,1,1-trichloroethane by infrared was of no practical value.

The subjective and physiological responses to 1,1,1-trichloroethane vapor noted during these exposures agree closely with those reported by Torkelson, *et al.*<sup>3</sup> There was a rapid onset of lightheadedness at atmospheric concentrations exceeding 900 ppm. Hence, in order to have a desirable margin of safety for prevention of accidental injury due to lightheadedness, the atmospheric concentration in the working environment should not exceed 500 ppm. The eye irritation experienced by 1,1,1-trichloroethane users is too mild to be relied upon as a good warning property of excessive exposure.

The laboratory data obtained indicate that these acute exposures produced no significant liver damage. The data adds support to previous studies which have indicated that 1,1,1-trichloroethane in high concentration acts as an anesthetic agent and has only slight capacity to cause reversible injury to liver or kidneys.<sup>3, 14</sup> Transient elevation of the urinary urobilinogen in two subjects following the anesthetic exposure suggests that 1,1,1-trichloroethane does exert an adverse effect upon liver function. However, none of the other liver function tests employed showed any change following the exposures. If a subject is chronically exposed to this compound it would seem advantageous to periodically check his urinary urobilinogen concentration for this laboratory test has proven to be the most sensitive index to liver stress produced by this type of compound.<sup>11</sup>

### Summary

A series of six controlled human exposures to 1,1,1-trichloroethane vapor was conducted. Using infrared spectrometric methods, the presence of the compound in blood during the exposures and the concentration of the compound in the expired air after the exposures were determined. 1,1,1-Trichloroethane was observed to give a prolonged exponential "decay curve" when its concentration in the postexposure expired air was plotted versus hours postexposure. This

"decay curve" was predictable enough to allow a reasonable estimation of the magnitude of exposure, 0.5 to 3 hours after the exposure had occurred. Therefore, the analysis of postexposure expired air allowed a positive identification of the compound, and provided data with which the magnitude of the exposure might be estimated.

Chemical, physiological, and clinical laboratory studies were carried out and correlated with the vapor exposures. The determination of the concentration of urinary urobilinogen proved to be the most sensitive test of liver stress produced by markedly excessive exposures to 1,1,1-trichloroethane. The laboratory studies and subjective responses which were noted lend further assurance that 500 ppm is a satisfactory threshold limit for this compound.

### Acknowledgments

The authors express their sincere appreciation to the volunteers who joined them in the exposure chamber: D. L. Cassiday, E. L. Garfield, H. Martin, E. H. Ode, V. K. Rowe, E. Murray, and P. Wright. The help of J. E. Peterson, B. H. Blake, D. Leavens, C. Licht, and C. Layne in preparing and analyzing the samples is gratefully acknowledged.

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#### RADIATION STANDARD

A NEW AMERICAN STANDARD specifying minimum requirements for the protection of workers from overexposure to radiation and radioactive dusts and gases in the uranium mining and milling industry has been approved by the American Standards Association. This publication *American Standard Radiation Protection in Uranium Mines and Mills (Concentrators) N7.1-1960* covers the mining, transporting and refining of ores to produce uranium concentrates suitable for the feed materials of production plants. Suggesting procedures for the proper control of the environment and examination of workers with a view toward protection from radiation, the standard is intended to serve as a guide for management and regulatory agencies having responsibility in this field of activity. In addition to offering definitions of all terms used, the standard specifies maximum permissible doses from external radiation, permissible concentrations of radioisotopes in air, hazards, management responsibility, medical supervision, protective measures and equipment, and transportation of ores. A five-part appendix, though not a part of the standard, deals with suggested procedures for measuring external radiation and atmospheric concentrations of radon daughters, for obtaining breath radon samples, for surveys of uranium concentrating mills, and the ventilation of uranium mines.

Twenty-one organizations including the Atomic Industrial Forum, Inc., and the National Safety Council, administrative sponsors, are represented on the ASA sectional committee which developed the standard. Participating for the government are the U. S. Atomic Energy Commission, U. S. Department of Labor, Bureau of Labor Standards, U. S. Public Health Service, and National Bureau of Standards.

Copies of the standard, N7.1-1960, which sell for \$2.00 each, are available from the ASA, Department PR 211, 10 East 40th Street, New York 16, New York.

# The Toxicity of Boron Trifluoride when Inhaled by Laboratory Animals

T. R. TORKELSON, M.S., S. E. SADEK, Ph.D., D.V.M.,  
and V. K. ROWE, M.S.

*Biochemical Research Laboratory, The Dow Chemical Company,  
Midland, Michigan*

Rats, rabbits, and guinea pigs were exposed seven hours per day, five days per week for periods up to six months duration to atmospheres containing boron trifluoride in concentrations calculated to be 12.8, 7.7, or 3.0 ppm. Analysis showed concentrations to be about one-half of these levels. The major effect of repeated inhalation was respiratory irritation causing injury ranging from death to a slight increase in pneumonia. On basis of the study, a value of 0.3 ppm is tentatively suggested as a threshold limit value for boron trifluoride.

## Introduction

BORON trifluoride,  $\text{BF}_3$ , is generally handled as a compressed gas (BP =  $-101.9^\circ\text{C}$ ). If allowed to escape to the atmosphere it very rapidly unites with moisture to form a white fog. Although the fog is irritating to the skin and eyes the primary hazard is probably from inhalation. Since this fog has an acidic odor, concentrations which are injurious from single exposures are obvious to the senses, if not painful. Stokinger and Spiegl<sup>1</sup> reported that a 5.5-hour exposure to 750 ppm resulted in death to 10 of 10 guinea pigs, 1 of 10 mice and 1 of 10 rats. A 1.4-hour exposure of 10 guinea pigs to 350 ppm resulted in death of seven. A 10.9-hour exposure to 135 ppm resulted in death of 1 of 10 guinea pigs and none of 10 rats and mice. Deaths were the result of pulmonary irritation. Surviving animals were reported to have quickly regained any loss in weight.

The only report of experiments to determine the effects of repeated inhalation of boron trifluoride is also by Stokinger and Spiegl.<sup>1</sup> Rats, rabbits, mice, guinea pigs, dogs and cats were exposed 6 hours per day, 6 days per week for 30 days to either 100 ppm or 15 ppm  $\text{BF}_3$  in air. Their summary of results is quoted:

"Two inhalation-exposure studies of animals at 100 and 15 ppm  $\text{BF}_3$  vapor for 30 days suggest that this compound is a pulmonary irritant predisposing the animals to pneumonia. Inhalation of  $\text{BF}_3$  vapor also produced dental fluorosis.

"The essential toxicological findings were:

1. All the animals of six species died or were sacrificed in a moribund condition at 100 ppm; few died at 15 ppm.
2. At the higher level, weight response was subnormal.
3. Definite histopathological pulmonary changes were noted in dogs and rats exposed to 100 ppm. Very mild renal-tubular degeneration occurred in rats.
4. The only biochemical abnormality noted was a decrease in serum inorganic phosphorus immediately prior to death.
5. Hematological changes were not significant.
6. The degree of dental hypoplasia paralleled the quantity of fluoride in the teeth of exposed rats."

Because of the limited duration of the previously discussed experiments, it was thought desirable to expose animals for several months in order to evaluate the possibility that organic injury other than pulmonary irritation might develop from such exposure. The data to be presented will include the results of 3 separate experiments in which laboratory animals were exposed 7 hours per day 5 days per week to concentrations in air calculated to be 12.8, 7.7 or 3 ppm of  $\text{BF}_3$ .

## Experimental Procedures

### Material Studied

The samples used in these studies were obtained commercially.<sup>2</sup> No attempt was made to determine the purity of the samples.

### Exposure Chambers and Metering Equipment

Because of the rapidity with which  $\text{BF}_3$  in ordinary air unites with moisture to form droplets, it was necessary to add the dry  $\text{BF}_3$  gas directly into the exposure chambers in order to prevent loss in the ducts and pipes. No attempt was made to control the humidity other than the partial control given by the building air conditioning system. Generally the relative humidity was about 30%.

In the first two experiments (12.8 and 7.7 ppm nominal) the metering was done by means of a single syringe pump. Since this pump assembly held the syringe in an upright position, it was possible to use a mercury seal to prevent moisture from entering between the barrel and the plunger of the syringe. After filling each morning, the 100 ml syringe which was used had sufficient capacity to deliver the chemical for the entire 7-hour exposure without refilling. The metering equipment was held in a constant temperature pump house at  $30^\circ\text{C} \pm 1^\circ\text{C}$ . The  $\text{BF}_3$  was conducted from the syringe by 1-mm ID glass tubing to the top of a 160-liter cubical exposure chamber which has been described previously.<sup>3</sup> The capillary tubing entered concentrically into a  $\frac{1}{2}$ -inch ID glass tube through which was flowing dry (pre-purified) nitrogen gas. The dry nitrogen gas blew the  $\text{BF}_3$  out into the inlet air stream far enough so that the particulates resulting from the union of  $\text{BF}_3$  with moisture did not plug the end of the capillary delivery tube. The nitrogen was generally kept flowing day and night to prevent condensation of moisture on the glassware. The flow of nitrogen was small enough so that hypoxia was not a factor. In order to eliminate as many obstructions to the particles as possible, the rats were not caged during exposure but allowed freedom of the chamber. The guinea pigs were confined in expanded metal cages. The air flow through the chamber was 16 liters per minute in the first experiment and 26.6 liters in the second. The flow of  $\text{BF}_3$  was 0.204 ml per minute in each experiment making theoretical concentrations of 12.8 and 7.7 ppm  $\text{BF}_3$  added to the chamber atmosphere. The flow of nitrogen was 0.5 liters/minute.

Air samples were taken by inserting a fritted glass scrubber directly into the chamber through a port on the top of the chamber.

In the third experiment a large rectangular vault type chamber was used.<sup>4</sup> This 3700 liter capacity stainless steel chamber was constructed primarily for exposure to vapors but appeared to function well when used for the particulates formed from  $\text{BF}_3$ . Two hinged doors sealed with Silastic<sup>®</sup> gasketing opened from a center mullion

to permit two racks of cages to be rolled into the chamber. The racks and cages which were also constructed of stainless steel contained the experimental animals.

The containers of food and water were removed from cage racks prior to exposure to prevent contamination by absorption of  $\text{BF}_3$ . Clean trays for the animal wastes were put in place. The racks of cages were rolled into the chambers, the doors closed and the desired exposure given. After exposure the racks were removed from the chamber, rolled into the animal room and the animals given food and water.

The  $\text{BF}_3$  and air inlets to the chamber were located at the top behind a 4-bladed, 24 inch, 173 rpm fan to prevent channelling of air in the chamber.

The  $\text{BF}_3$  was metered by displacement, Figure 1. A 500 ml graduated separatory funnel was used as a reservoir for the  $\text{BF}_3$ . Mineral oil was pumped into the flask by means of a Dual Syringe Feeder<sup>5</sup> pump to displace the  $\text{BF}_3$ . Fresh mineral oil was used each day. The mineral oil became slightly discolored but did not dissolve a significant amount of  $\text{BF}_3$ . The displaced  $\text{BF}_3$  was conducted to the chamber through capillary glass tubing connected to the dispersing equipment, Figure 2. Prepurified nitrogen was used to shield the capillary outlet as in the previous experiments. The metering equipment was held in a constant temperature pump house at  $30 \pm 1^\circ\text{C}$ .

In practice the reservoir was filled by closing stopcocks A and C. Stopcock B and the valve of the cylinder were then opened. When a few ml of  $\text{BF}_3$  had escaped through the mercury seal in the suction flask, the oil in the separatory funnel was drained through stopcock D. When sufficient oil was drained, stopcock D was closed and a small amount of  $\text{BF}_3$  again allowed to escape through the mercury seal. (The mercury seal allowed a ready escape for any undue pressure which might be released from the cylinder and also assured that the pressure in the filled reservoir would not exceed  $\frac{1}{2}$ " Hg, the depth of the mercury seal.)

Stopcock B was then closed and stopcocks A and C opened and the metering pump turned on.

As can be seen in Figure 2 the mixing and dispersing assembly was constructed of glass. The dry  $\text{BF}_3$  from the metering assembly entered into the top of the innermost of 3 concentric tubes. Dry (pre-purified) nitrogen was admitted through the second tube ( $\frac{1}{2}$ -inch OD). This shielded the tip of the  $\text{BF}_3$  outlet from moisture and helped to blow the  $\text{BF}_3$  out into the air stream entering through the 2-inch OD outer



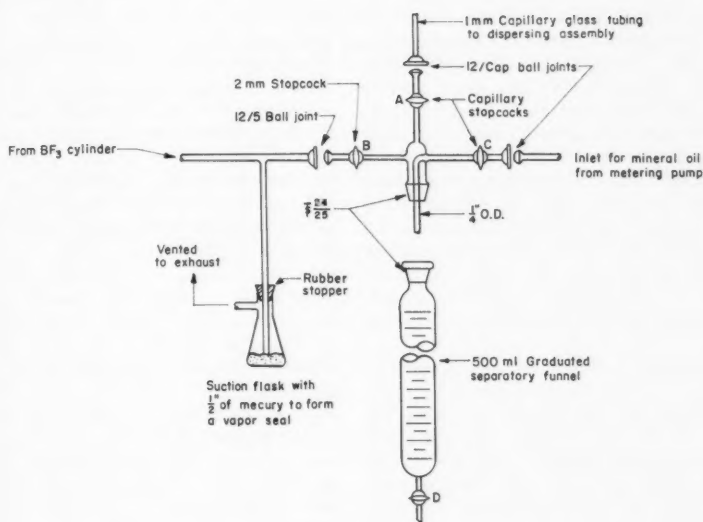


FIGURE 1. Gas displacement assembly for metering boron trifluoride.

tube. This assembly worked very satisfactorily during the entire 3rd phase of the experiment and may have application in metering other moisture sensitive gases.

#### Analysis of the Chamber Atmosphere

Boron trifluoride unites with the moisture in air to form a white fog or mist. It was demonstrated by infrared absorption that essentially all of the  $\text{BF}_3$  reacted with moisture and was removed from the gaseous phase. When 50 ppm of  $\text{BF}_3$  was added to dry air, it was easily detected by infrared absorption in a 10 meter cell whereas 100 ppm  $\text{BF}_3$  added to room air was not detectable. Apparently, it had been removed from the vapor phase by reaction with moisture. The products of moisture and  $\text{BF}_3$  are not clearly defined in the literature. It might be assumed that the first step in mixing  $\text{BF}_3$  with moist air would result in a hydrate. However, it was evident that some hydrolysis also occurred since slight etching of the dispersing glassware was seen. The products of this hydrolysis were not determined, but the etching indicates that fluoride ion was present. A white solid was seen in the exhaust portion of the exposure equipment.

Analyses of the chamber atmospheres were made by drawing air samples through a fritted glass scrubber containing 25 ml of distilled water. The scrubber was outside the chamber and the sample drawn through a short length of straight glass tubing which extended through a

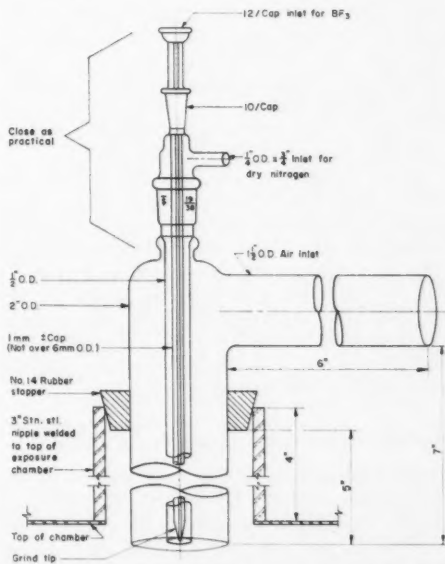


FIGURE 2. Mixing and dispersing assembly for boron trifluoride.

port in the side of the chamber. The sample was then transferred to a 50-ml volumetric flask with repeated and thorough rinsings. After diluting to volume the sample was mixed by inversion and transferred to a polyethylene bottle until

subsequently analyzed by a carminic acid technique.<sup>6</sup> A fritted glass scrubber was shown to be essentially 100% efficient by putting two scrubbers in series. The first scrubber was found to contain all the boron, the second scrubber essentially none. A fritted glass scrubber was found to be more efficient for  $\text{BF}_3$  in moist air than a midjet impinger and distilled water was found to be better than 1% KOH in ethanol as a scrubbing solution. The sampling rate was varied from one-half to three liters per minute with no loss of sampling efficiency. Samples of room air (blanks) were shown to be essentially nil indicating no appreciable leaching of boron from the glass.

Since it was not known what compounds of boron were present in the atmosphere all analyses were made for total boron and were expressed as  $\text{BF}_3$  for lack of better identification. The analytical values during exposures to the nominal concentration of 3 ppm ranged from 0.76 to 2.3 ppm with an average of 1.5 ppm  $\text{BF}_3$ .

Because the chambers used for these exposures were not designed for exposures to particulate materials, samples were taken at several points within individual cages where the animals were, to check the distribution of the  $\text{BF}_3$ . These values were found to range randomly from 0.9 to 1.3 on the first trial and from 0.8 to 1.2 on the second trial indicating reasonably good distribution throughout the chamber cages.

In an attempt to measure the particle size with a Bausch and Lomb darkfield micro dust-counter, it was noted that the droplets were very uniform in size, about one micron in diameter. This was subsequently discovered to be the result of continued absorption of water by the droplets after impingement. Hence, this measuring technique, though it did not accurately define the particle size, did indicate that the particles were less than one micron in size.

#### *Animals Exposed and Experimental Protocol*

The animals used in this study were from the stock colonies of the laboratory. The rats and rabbits received a commercial laboratory diet.<sup>7</sup> The guinea pigs were fed a guinea diet<sup>7</sup> during the first and second experiments. During the third experiment, they were changed to regular laboratory diet supplemented with cabbage as a source of vitamin C. All groups were carefully matched as to age, weight, number and condition with control groups.

In the first experiment ten male guinea pigs and fourteen female rats were exposed seven hours per day to a nominal concentration of 12.8

ppm. The guinea pigs appeared normal until about one month after exposures started, then deaths ascribed to respiratory failure or asphyxia began to occur. Deaths occurred during or after the nineteenth, twenty-fourth, twenty-fifth (3), thirtieth and forty-second exposures. One rat died after 34 exposures in 49 days. The cause of death was not determined. The surviving guinea pigs and four rats were sacrificed by decapitation and autopsied after 42-45 exposures in 62-65 days. Samples of blood, bone, lung, liver, kidney and teeth were saved for chemical analysis of fluoride, Table I. The lungs, heart, liver, kidneys and spleen were weighed. These organs as well as the pancreas and adrenals were fixed, and stained in hematoxylin-eosin for microscopic examination. Four more rats were sacrificed after sixty exposures in 87 days and examined for gross and micropathological changes. Exposures were stopped and the remaining rats X-rayed, pastured one month and then killed and examined grossly.

In the second experiment five female rats and ten male guinea pigs were exposed seven hours per day, five days per week to a nominal concentration of 7.7 ppm (3-4 ppm by analysis). The male guinea pigs showed considerable individuality in response. Deaths occurred after or during the second, sixth, seventh, and tenth exposures. The remaining six guinea pigs received a total of 28 exposures in 41 days, and although obviously uncomfortable because of respiratory irritation, they continued to grow until the 29th exposure. At this point in the experimental routine, a faulty flowmeter resulted in excessive concentrations of  $\text{BF}_3$  and  $\text{N}_2$ , sufficiently high to cause the death of all the guinea pigs but not high enough to seriously affect the rats. Postmortem examinations of two of the guinea pigs revealed no changes in the lungs grossly. The rats were sacrificed after 33 exposures in 51 days. The teeth were examined grossly for evidence of fluorosis and the teeth and bone analyzed chemically for fluoride.<sup>8</sup>

In the third experiment a group consisting of twelve male and twelve female rats, ten male and ten female guinea pigs, and three male and three female rabbits were exposed 127-128 times in 182-183 days to a nominal concentration of 3 ppm (1.5 ppm average by analysis). A similar group of unexposed controls were maintained. Mortality and weight records were kept for each animal. All animals were killed on the day following their last exposure. The rats were starved overnight and they and all the other animals were killed by decapitation. The animals were examined grossly for pathological changes. The heart, lungs, liver, kidneys, spleen and testes

TABLE I  
Average Fluoride Concentrations in Organs of Animals that Received Repeated  
7-hour Exposures to Boron Trifluoride

Species	Sex	Conc. ppm	Number of Exposures	Number of Animals	Average Fluoride Content in PPM				
					Teeth	Bone	Lung	Liver	Blood
Guinea pig	M	0	0	3	308	430	4.6	1.2	0.9
		12.8 (nominal)	42	5	441	882	4.9	1.1	2.5
Rat	F	0	0	4	502*		9.9	1.8	4.7
		12.8 (nominal)	45	4	738*		11.9	1.4	3.9
Rat	F	0	0	5	342	996			
		3-4	33	5	643†	1154			
Rat	F	0	0	4	580	1335			
		1.5	127	4	867‡	1732			
	M	0	0	4	305	735			
		1.5	127	4	506‡	1109			

\* X-rays of these rats showed no apparent changes in the bone structure.

† No gross changes characteristic of fluorosis of the teeth were seen.

‡ These teeth were lighter in color, characteristic of very mild fluorosis.

were removed and weighed. Those organs together with the pancreas and adrenals were fixed and then stained with hematoxylin-eosin for microscopic examination. The lower jaws of the rats were examined for evidence of fluorosis, stripped of flesh, measured, and saved for chemical analysis for fluoride.

Because of several deaths due to extraneous causes, an additional group of six female guinea pigs were exposed 88 times in 127 days to the same concentration. Unexposed controls were maintained. Body weight and mortality records were kept and gross pathological examinations were made at autopsy.

### Results of Animal Exposures

#### Repeated Exposure to a Nominal Concentration of 12.8 ppm $BF_3$

Guinea pigs were much more adversely affected by inhalation of air to which  $BF_3$  had been added than were rats receiving simultaneous exposures. Only one of fourteen female rats died during 45 seven-hour exposures in 65 days, whereas seven of ten male guinea pigs died as a result of the same exposures. Great individuality in response of the guinea pigs was noted. The guinea pigs showed obvious difficulty in breathing and appeared asthmatic. Deaths were the result of respiratory irritation and asphyxia. Pneumonitis, suggestive of chemical damage, was

seen in the hilar regions of the guinea pig lungs and the lung weights were increased, Figure 3 and Table II. All other organ weights were normal. Microscopically, the vessels in the alveolar walls were distended with red blood cells and the alveoli contained many erythrocytes. Phagocytic cells containing yellow material were also present. The alveoli walls were thickened and separated from the vascular epithelium. Areas of collapse and emphysema were observed in the lung areas adjacent to the most severely affected lesions.

The rats that received 45 exposures in 65 days were normal when judged by their appearance, mortality and organ weights. Gross and microscopic changes indicative of chemical irritation were seen in the lungs. The hilar regions were most obviously effected. Microscopically, the injury was manifested as pneumonitis. The four rats killed after 60 exposures in 87 days also showed pathological changes in the lungs. X-rays of the whole bodies of the rats showed no differences from the controls attributable to the exposures. The five rats which were pastured for one month after exposures were ceased, continued to grow and gain weight and were normal in appearance. No evidence of irritation of the feet due to contact with the cage bottoms was noted in any of the studies. However, the amount of fluoride ion ingested due to licking of the fur and skin may have been contributory to the fluorosis seen in the teeth and the increased fluoride content of the tissues.

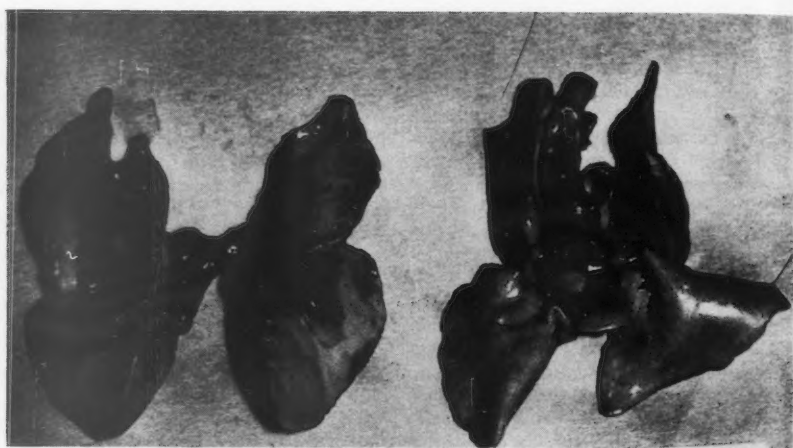


FIGURE 3. Guinea Pig Lungs. The lung on the left is from a guinea pig which received 42 seven-hour exposures in 62 days to a calculated concentration of 12.8 ppm  $\text{BF}_3$  in air. The lung on the right is from an air exposed control.

TABLE II

Summary of Average Body and Organ Weights of Animals Receiving Repeated 7-hour Exposures to 12.8 ppm Boron Trifluoride in Air 5 Days per Week

Species	Sex	Group	Exposures	Ratio Surviving Animals/Treated Animals	Final Av. Body Wt. Grams	Organ Weights, g/100 g Body Weight					
						Lung	Heart	Liver	Kidney	Spleen	Testes
Rat.....	F	Exposed	45	13/14	216	0.63	0.31	2.73	0.72	0.33	
Rat.....	F	Control	0	14/14	229	0.65	0.37	2.96	0.83	0.35	
Guinea pig.....	M	Exposed	42	3/10*	694	0.80†	0.34	3.37	0.71	0.13	0.50
Guinea pig.....	M	Control	0	10/10	592	0.64	0.29	3.20	0.67	0.20	0.54

\* One guinea pig which died during the 42nd exposure was decapitated, drained of blood and its organ weights are included in the averages for this group.

†  $P = .001$ .

#### Repeated Exposure to a Nominal Concentration of 7.7 ppm $\text{BF}_3$

Five rats exposed 33 times in 51 days to 7.7 ppm (3-4 ppm  $\text{BF}_3$  by analysis) were normal in appearance and growth and no evidence of fluorosis was seen in the teeth. The fluoride content of the teeth and bones was increased (Table I).

Again the guinea pigs receiving simultaneous exposures were much more adversely affected than the rats. Deaths occurred during the second, fifth, sixth and eleventh exposures. The deaths were accompanied by what appeared to be an asthmatic attack. The six surviving guinea pigs continued to grow through 28 exposures although they were obviously uncomfortable and had difficulty breathing. They were killed acci-

dentally during the 29th exposure as described previously.

#### Repeated Exposure to a Nominal Concentration of 3 ppm $\text{BF}_3$ (1.5 ppm by Analysis)

The rats, guinea pigs, and rabbits receiving repeated seven-hour daily exposures for six months to an average concentration of 1.5 ppm  $\text{BF}_3$  in air (by analysis) were only minimally affected. Growth, appearance and mortality were normal for all groups with the exception of the female guinea pigs. Four of the ten guinea pigs died, however, the deaths were attributable to extraneous causes. The second group of six female guinea pigs received 88 exposures in 127 days. They appeared normal and no deaths oc-

TABLE III

Summary of Average Body and Organ Weights of Animals Receiving Repeated 7-hour Exposures to 1.5 ppm of Boron Trifluoride in Air 5 Days per Week for Six Months

Species	Sex	Treatment	No. of Surviving Animals	Final Av. Body Wt. Grams	Organ Weights, g/100 g Body Weight					
					Lung	Heart	Liver	Kidney	Spleen	Testes
Rat.....	M	Unexposed	9	350	0.51	0.31	2.69	0.69	0.22	0.81
Rat.....	M	Exposed	8	347	0.59*	0.31	2.61	0.69	0.19	0.83
Rat.....	F	Unexposed	9	212	0.67	0.40	3.04	0.83	0.27	
Rat.....	F	Exposed	12	216	0.68	0.37	2.91	0.78	0.24	
Rabbit.....	M	Unexposed	3	3160	0.35	0.23	1.80	0.46	0.03	0.18
Rabbit.....	M	Exposed	3	3210	0.38	0.21	2.01	0.47	0.03	0.19
Rabbit.....	F	Unexposed	3	4130	0.41	0.18	1.87	0.45	0.03	
Rabbit.....	F	Exposed	3	3960	0.31	0.20	1.97	0.40	0.03	
Guinea Pig.....	M	Unexposed	10	920	0.56	0.29	3.50	0.69	0.12	0.52
Guinea Pig.....	M	Exposed	9	970	0.54	0.26	3.65	0.62	0.09	0.47
Guinea Pig.....	F	Unexposed	9	864	0.68	0.28	4.38	0.72	0.17	
Guinea Pig.....	F	Exposed	6	787†	0.72	0.30	4.44	0.68	0.15	

\*  $P = 0.24$ .

†  $P = 0.22$ .

curred but the final average body weight was below that of the controls 723 g vs 855 g. However the wide range of weights made the finding not significant statistically ( $P = 0.073$ ). When sacrificed, no pathological changes were seen. Histopathological examinations were not made of this group.

Gross observation at autopsy and the average weights of the organs of the rats, rabbits and guinea pigs revealed no abnormalities, Table III. Microscopically, it appeared that the rats were very slightly affected. Pathological changes characterized by the presence of areas of pneumonitis, peribronchiol round cell infiltration and areas of congestion of the capillaries lining the alveolar walls were seen. Guinea pigs exposed to 1.5 ppm appeared to have a slightly higher incidence (30%) of pneumonitis. When examined for micropathological changes, the rabbits did not differ significantly from the controls.

The teeth of the male and female rats which were examined for fluorosis were lighter in color than the controls. This finding is of doubtful significance since the teeth appeared sound and as hard as the controls. The average length of the exposed incisors was measured and found to be the same for the exposed and the control groups (males 13 mm, females 11 mm). The average length of the jaw bones was similar as well.

This concentration was detectable by the per-

sonnel handling the animals as a rather pleasant acidic odor.

### Discussion

It appears that the primary hazard of over-exposure to  $BF_3$  is irritation of the respiratory tract. The only other adverse effect attributable to the chemical exposure was fluorosis of the teeth. The likelihood of detrimental effect on the teeth of adult workers appears to be remote, but the use of urinary fluoride level as well as environmental measurements may be proper for environmental control purposes.

These findings agree qualitatively with those published by Stokinger and Spiegel,<sup>1</sup> but the present data indicates a higher degree of toxicity than reported by these workers.

It is of interest to compare the strikingly greater sensitivity of guinea pigs as compared to rats. Although the rats undoubtedly received a greater exposure to the nominal concentrations of 12.8 and 7.7 ppm because they were not caged but free to sniff the incoming undiluted gas, they were much less effected. This species difference was not evident in rats and guinea pigs exposed to 1.5 ppm. The greater sensitivity of guinea pigs to  $BF_3$  was also reported by Stokinger and Spiegel<sup>1</sup> and probably results from the reported susceptibility of guinea pigs to respiratory irritants.<sup>2</sup>



There is a very apparent discrepancy in the number of exposures causing deaths to guinea pigs exposed to 12.8 and 7.7 ppm. Guinea pigs exposed to the lower concentration, 7.7 ppm, died after fewer exposures than those exposed to the high concentration. No definite explanation can be made. However, humidity was not controlled and it is possible that differences in humidity may have been a factor in determining the particle size of the mist, hence its toxicity. It was noted that on humid days, the guinea pigs appeared to be more uncomfortable than on less humid days. The great individual variation between guinea pigs may have been a factor as well.

In considering a threshold limit value for industrial hygiene purposes, these data certainly indicate that the level should be below 1 ppm. The authors are of the opinion that there would be little hazard to ordinary individuals even on repeated and prolonged exposure to 0.3 ppm  $\text{BF}_3$  based on analysis for boron. In view of the asthmatic-like response which was observed in guinea pigs exposed to  $\text{BF}_3$ , it would seem unwise to us to employ persons with known asthmatic conditions in jobs involving exposure to this gas.

A concentration of 1.5 ppm was found to be detectable by smell but it did not offer sufficient warning properties to limit over exposure. Hence analysis of the air in the working environment is recommended for control purposes.

### Summary

Rats, rabbits and guinea pigs were exposed 7 hours per day, five days per week for periods of up to 6 months duration to atmospheres to which boron trifluoride was added to give concentrations calculated to be 12.8, 7.7 or 3 ppm.

Analysis based on total boron indicated actual concentrations of about one-half these levels.

The major effect of repeated inhalation was respiratory irritation which resulted in pneumonitis apparent at all concentrations studied. The higher concentrations caused deaths in guinea pigs after repeated exposure. Evidence of fluorosis of the teeth was also detected.

A standard for evaluating repeated seven to eight-hour daily exposures may be defined as the concentration below which practically all analytical results must fall. On the basis of this definition, the value of 0.3 ppm is tentatively considered to be an appropriate standard for boron trifluoride.

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# Sample Collection Techniques for Combustion Sources—Benzopyrene Determination

ROBERT L. STENBURG, B.S., M.P.H., DARRYL J. von LEHMEN, B.Ch.E., and ROBERT P. HANGEBRAUCK, B.S.

*Robert A. Taft Sanitary Engineering Center, Public Health Service, Cincinnati, Ohio*

In evaluating combustion processes for their contribution of benzo(a)pyrene and other potential carcinogens to the atmosphere, the materials of interest may be lost during sampling unless the collection temperature is controlled. Cooling of the gases under both wet and dry conditions has been tried. This study demonstrates that collection of benzo(a)pyrene from high temperature gas streams can be effectively accomplished by filtration after cooling the gas stream to or near ambient temperatures. A series of water bubblers and condensate traps immersed in an ice-water bath, followed by a high efficiency filter proved to be a satisfactory technique.

THE role of various hydrocarbon compounds in producing chemically-induced animal cancers has been well established by an impressive number of reported studies (Hartwell, 1957; Haddow, 1958). Many investigators have shown benzo(a)pyrene to be one of the more active carcinogens. A recent publication by Sawicki, *et al.*,<sup>1</sup> reporting the extent of benzo(a)pyrene (also called 3,4-benzopyrene) associated with particulate matter collected from the air of several major cities, emphasizes the importance of knowing more about the occurrence of this and other related polynuclear hydrocarbons having demonstrated or presumed carcinogenic significance.

Such polynuclears are formed as combustion by-products during the burning of conventional fuels (coal, oil and gasoline) and cellulose materials such as wood, paper, and tobacco. Potential sources releasing these materials to the atmosphere include domestic and industrial heating processes, automobile engine exhausts, incinerators burning wood, paper, cardboard and other organic material contained in municipal and industrial wastes, and certain specialized industrial processes such as coke, carbon black and petrochemical production, and industries producing or processing coal tars.

The extent to which benzo(a)pyrene and other polynuclear hydrocarbons are emitted to the atmosphere from some of the more commonly occurring suspect sources is currently

being evaluated in a source sampling study by the Public Health Service. A first step in this study was the development of a technique for collecting samples from high temperature combustion and process gas streams in a manner which would assure retention of the hydrocarbon materials of interest. This paper reports the findings of a series of tests conducted (1) to develop suitable methods for cooling the gas samples, (2) to establish temperature requirements for the collected sample during the sampling period, and (3) to evaluate wet versus dry collection techniques.

With a melting temperature of 180°C and a boiling point near 500°C, benzo(a)pyrene exists in the atmosphere in the solid phase, usually adsorbed on solid particles which can be recovered from the air by filtration.<sup>2</sup> However, in process gas streams the material may be either solid, liquid or gaseous depending on the temperature at the sampling point. Commins and Lawther<sup>2</sup> have demonstrated that benzo(a)pyrene will remain on a filter during sampling when the filter temperature does not exceed 65°F.

These factors dictated the necessity of using a sampling technique which would cool the sample gas stream prior to collecting the condensed and adsorbed material by filtration. Size of the sampling equipment was dictated by requirements of the sampling program which called for 300 to 400 cu ft samples in order to assure obtaining comparative data from relatively low concentration sources. To avoid unduly long sampling periods, the equipment was designed to

<sup>1</sup>Presented at the Twenty-second Annual Meeting of the American Industrial Hygiene Association, Detroit, Michigan, April, 1961.

handle flows ranging up to 3.0 scfm. (Standard conditions are 70°F, 29.92 in. Hg.)

### Experimental Procedure

Samples obtained to date were collected from two combustion sources. These were (1) the stack of an experimental incinerator burning a mixture of newspaper and asphalt felt roofing under controlled combustion conditions, and (2) the exhaust pipe of an automobile operated under controlled conditions on a chassis dynamometer. Simultaneous samples were taken on all but two tests by splitting the sample gas stream into two equal fractions and subjecting each fraction to different collection conditions.

Two methods of cooling the sample gas stream were investigated: (1) by passage through a straight tube metal condenser cooled with circulating ice water prior to collection of the particulate on a filter, hereafter called the dry collection technique, and (2) by passage through a series of water bubblers and condensate traps prior to the final filter collector, hereafter called the wet collection technique. Both sampling trains are shown in Figure 1.

Stainless steel pipette sterilizing cans (2½" diameter x 12" long) were used for the bubblers and condensate traps, all of which were interconnected with 7/16" I.D. stainless steel tubing. These components were followed by a glass fiber filter (MSA type 1106-BH) held in a stainless steel housing and supported by a porous stainless steel plate.

After a very few tests, it became obvious that the dry collection technique, although relatively effective in cooling the gas stream to the desired temperature, had a number of operational limitations, the most serious of which involved difficulty in recovering that portion of the sample which condensed on or adhered to the condenser tube. Because of this and other drawbacks, work with this technique was discontinued and effort was concentrated on further development of the wet collection technique. A distinct advantage of this latter technique is its greater flexibility in adjusting to wide temperature variations encountered in a field sampling program. Increased cooling capacity can be achieved simply by adding extra bubblers to the existing train.

A series of tests involving both an uncooled filter and wet collection system elements was made to evaluate the suitability of the various combinations of bubblers, condensate traps and filters shown in Figure 2. Samples were collected from the exhaust of a dynamometer-mounted automobile while road load, manifold vacuum and engine rpm were held constant. Each test involved a different combination of operating conditions. Collection train No. 1 was used as the standard collector on all tests, and results from other collection trains are compared to results obtained with this train. Temperature of gas flowing through the final condensate trap immersed in the dry ice-acetone bath on train No. 1 was held between 34° and 38°F. In passing from this condensate trap to the filter, the gasses

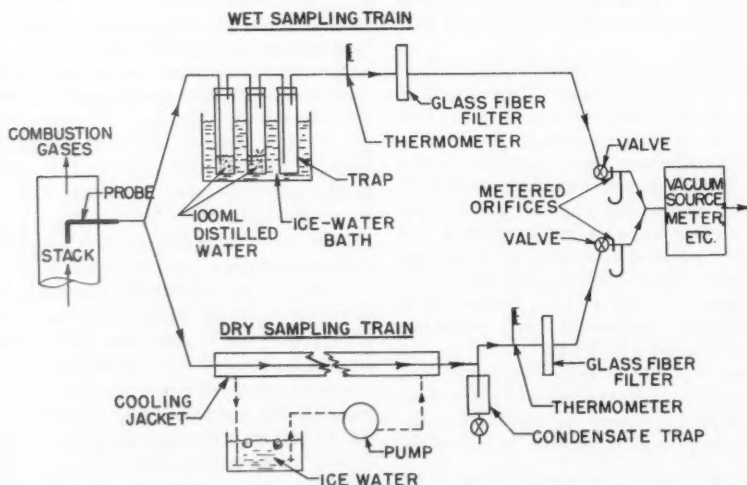


FIGURE 1. Schematic diagram of split-flow sampling apparatus used to determine relative collection efficiencies for benzopyrene.

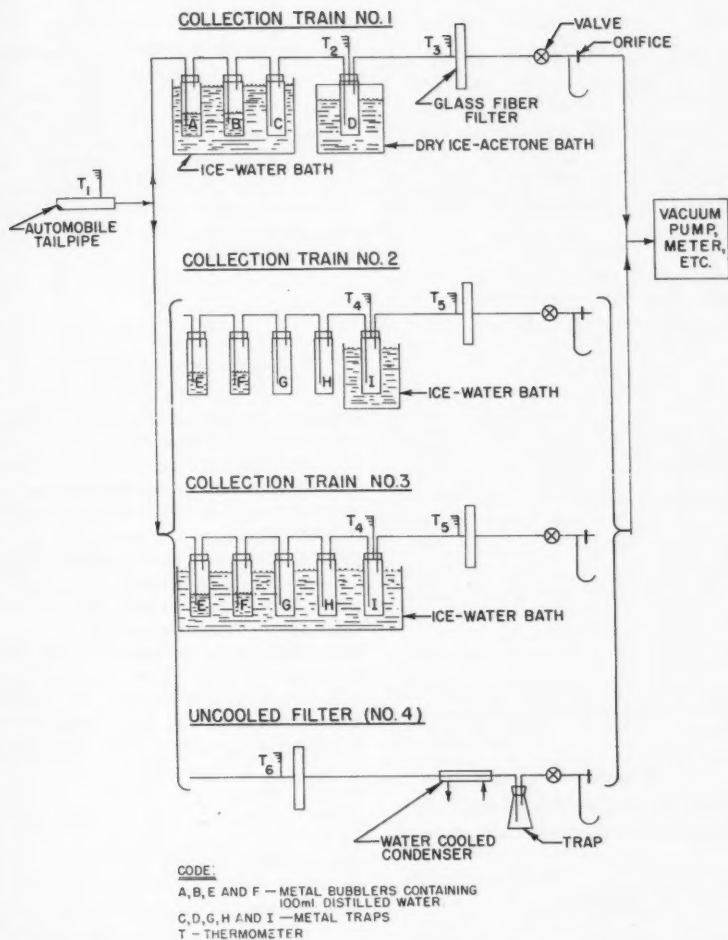


FIGURE 2. Various methods used for collecting polynuclear hydrocarbon samples from automobile exhaust.

warmed sufficiently to produce a filter temperature between 55° and 60°F which is below the temperature at which Commins and Lawther<sup>2</sup> showed no loss of benzo(a)pyrene. The other collection trains ranged from conditions of no cooling (No. 4) to ice water cooling of one or all bubblers and traps (Nos. 2 and 3).

In processing the collected samples, solid matter was removed from liquid contained in the bubblers and condensate traps by filtering through glass fiber filters (MSA type 1106-BH) which were then allowed to dry at room temperature. Benzene extractions were made of both the water collected fraction and the filter

collected fraction, and all containers from the sampling train were rinsed with redistilled benzene. Subsequent evaporation of the benzene was carried out at room temperature by passing a stream of nitrogen over the surface of the samples.

The analytical procedures followed in determining concentration of benzo(a)pyrene in the samples was similar to that described by Sawicki, *et al.*,<sup>3</sup> in analyzing atmospheric collected particulates for benzo(a)pyrene content. The modifications necessary to adapt this technique to the analysis of source samples will be detailed in a later publication.

## Results

Results of tests made to compare the wet and dry collection techniques depicted in Figure 1 are shown in Table I. Although the number of tests made was insufficient to definitely establish the relative collection efficiencies of the two methods, the data does confirm the fact that benzo(a)pyrene can be recovered by either col-

TABLE I

Results of Collecting Benzo(a)pyrene from Incinerator Flue Gas by Wet and Dry Sampling Techniques

Incinerator Operating Conditions		Sampling Train Conditions			Sampling Train Used*	Benzo(a)-pyrene Collected ( $\mu\text{gm}/1000 \text{ meters}^3$ of gas)
Excess combustion air	Flue gas temp. (°F.)	Filter temp. (°F.)	Sampling rate (scfm)	Volume of gas sampled (scf)		
70%	1760	63	2.0	91	Wet	5500
		71	2.0	91	Dry	5900
70%	1700	64	2.0	152	Wet	4400
		72	2.0	152	Dry	1600
200%	1055	68	2.0	111	Wet**	0
		71	2.1	116	Dry**	0

\*—See Figure 1 for details of wet and dry sampling trains.

\*\*—These were individual rather than simultaneous samples.

TABLE II

Effect of Varying Filter Temperature on Collection of Benzo(a)pyrene from Auto Exhaust

Auto-mobile Test Condition	Gas Temp. at Tailpipe (°F.)	Sampling Train Conditions			Sampling Train Used*	Benzo(a)-pyrene Collected ( $\mu\text{gm}/1000 \text{ meters}^3$ of gas)
		Filter temp. (°F.)	Sampling rate (scfm)	Volume of gas sampled (scf)		
3	560	58	1.19	201	No. 1	970
		300	1.19	201	No. 4	580
4	300	57	1.0	202	No. 1	7410
		95	1.0	202	No. 2	8160
6	165	61	1.0	132	No. 1	2600
		62	1.0	132	No. 2	2760
7	165	55	2.0	235	No. 1	4400
		132	2.0	235	No. 4	3700
8	155	58	1.0	140	No. 1	6170
		79	1.0	140	No. 3	6100

\*—See Figure 2 for details of sampling trains.

TABLE III

Comparison of Bubbler vs. Filter Collection of Benzo(a)pyrene

Benzo(a)pyrene Collected ( $\mu\text{gm}/1000 \text{ meters}^3$ of gas)	% Collected		
	On filter	In bubbler water and condensate	In benzene rinse of bubblers
2600	85	15*	—
2760	94	6*	—
970	65	33	2
7410	84	9	7
8160	91	3	6
4400	77	9	14

\*—Includes benzene rinse of bubblers.

lection technique, if and when the gas stream being tested contains the material of interest. On the first test, the condenser-cooled sample showed 7% more benzo(a)pyrene than the simultaneously collected bubbler-cooled sample, but the duplicate test had 64% less benzo(a)pyrene in the condenser sample. Time did not permit making additional tests to establish the reason for this variation. The decision to develop the wet collection technique of gas cooling was based on the greater flexibility of the wet technique in adapting to the requirements of a field sampling program and on the operational disadvantages of the dry technique previously mentioned rather than on the above limited data.

Table II gives results of additional tests in which samples were collected in trains as depicted in Figure 2. In these tests, final collection filters were maintained at several different temperatures. Sample gas streams split into two equal portions produced filter temperatures ranging from 132° to 300°F on the uncooled portions, while the ice water-cooled portions of the gas streams produced filter temperatures ranging from 55° to 95°F. Samples collected on the uncooled filters (No. 4) showed less benzo(a)pyrene than the corresponding samples collected from the bubbler cooled portions of the gas streams. On test condition No. 3, the filter operated at 300°F showed only 60% of the benzo(a)pyrene collected on the corresponding low temperature filter maintained at 58°F.

Comparison of results from simultaneously collected bubbler-cooled samples (Test No. 4), in which one filter temperature was above room temperature (95°F) while the other was below room temperature (57°F), does not indicate any advantage for the lower collection temperature. Resulting differences in benzo(a)pyrene collected at different temperatures on this test are attributed to experimental error in the



sampling and analytical techniques. On tests where dual samples were both collected at approximately the same temperature (61° and 62°F) the benzo(a)pyrene recoveries showed relatively good consistency (see Test No. 6).

Results obtained from the separate analysis of filter-collected material and bubbler-collected material from the same train are shown in Table III and indicate that in most cases only a small portion of the benzo(a)pyrene was collected in the bubblers, the major portion being collected on the filter following the bubbler train.

The bubbler technique of sample collection was found to be satisfactory for continuous sampling for intervals exceeding three hours. Gas volumes in excess of 300 scf were collected and sampling rates up to 2.0 scfm were used. Samples collected at 2.0 scfm from a 1760°F gas stream were readily cooled to 64°F at the filter.

The only operational difficulty encountered with the bubbler train involved condensation of moisture on the filter with a resultant increase in pressure drop during sampling. Immersion of the final condensate trap in a dry ice-acetone bath (sampling train No. 1) proved highly effective in removing moisture from the gas stream at this point and served to eliminate this problem.

### Summary and Conclusions

These tests show that benzo(a)pyrene present in high temperature gas streams can be collected by filtration after cooling the gas to or near ambient temperatures. A series of water bubblers and condensate traps immersed in an ice water bath proved to be a satisfactory technique for

this purpose. However, use of a high efficiency filter as the final collector is absolutely necessary since the washing process in the bubblers may remove only a small percentage of the benzo(a)pyrene.

Filter temperature on the order of 300°F resulted in part of the benzo(a)pyrene being lost during sampling. Filter temperatures of 95°F and below gave generally comparable results. Since the work of Commings and Lawther<sup>2</sup> demonstrated that benzo(a)pyrene suffers little if any loss from the filter during sampling at a filter temperature of 65°F, it is assumed that the collection efficiency of source samples at or near this temperature should be close to 100%.

### Acknowledgments

The authors are indebted to Mr. Elbert C. Tabor and other members of the National Air Sampling Network Staff for extraction of the samples; to Dr. Eugene Sawicki for directing the analytical work, and to the following members of his staff: Mr. F. Fox for making the chromatographic separations, Mr. W. Elbert for doing the U.V. spectrophotometer analyses and to Mr. J. Meeker, who made the calculations.

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# Ultramicrodetermination of Mercury in Blood

MORRIS B. JACOBS, Ph.D., LEONARD J. GOLDWATER, M.D.,  
and HARRY GILBERT

*School of Public Health and Administrative Medicine,  
Columbia University, New York, New York*

The method involving cold digestion, extraction with dithizone, decomposition of the mercury dithizonate by heating, and estimation of the mercury vapor produced by ultraviolet photometry has been modified so that only 0.1 ml of blood is required. The method has also been modified by use of an electric furnace instead of a Bunsen burner combustion chamber. With the aid of these modifications concentrations of mercury in the millimicrogram (nanogram) range can be determined.

OUR studies on the absorption and excretion of mercury have been continued. In a prior communication, Jacobs, Yamaguchi, Goldwater, and Gilbert<sup>1</sup> reviewed the literature relating to the determination of mercury in blood and in biological materials in general and this review does not need repetition here. Since our previous publication, however, Gutenmann and Lisk<sup>2</sup> described their modified Schöniger<sup>3</sup> combustion and dithizone method with added mercury as a carrier and Truhaut and Boudene<sup>4</sup> detail a procedure for the estimation of mercury in biologic material which includes an acid digestion, a distillation step, and a titration of the mercury with a chloroform solution of di-beta-naphthylthiocarbazone.

Hemeon and Haines<sup>5</sup> have reported their method for the automatic sampling and determination of microquantities of mercury vapor. The vapor is trapped by filtration through an impregnated tape of an AISI smoke sampler; the tape is impregnated with iodine-potassium iodide solution. The mercury in the spot is dissolved out, precipitated on a piece of copper foil, and then estimated by heating to vaporize the mercury, and measuring the amount of vapor by ultraviolet spectrophotometry.

A variation of the method for blood developed at Columbia University has been adapted for use in determining the concentration of mercurial fungicides on apples and vegetables.<sup>6</sup>

The method presented here, as in our prior report, combines cold incomplete digestion, ex-

traction of the mercury with dithizone, decomposition of the mercury dithizonate by heat with the production of mercury vapor, and subsequent estimation of the mercury by ultraviolet photometry, however, the amount of blood used has been reduced to 0.1 ml, that is one tenth the volume used in our prior method; the order of the addition of the reagents has been changed, and a new combustion unit has been employed. The method has been found adequate for the determination of concentrations of  $10^{-8}$  gram of mercury, that is of the order of millimicrogram (nanogram) concentrations of 0.1 ml of blood.

## Equipment and Reagents

### Apparatus

The apparatus consists of a furnace, Figure 1, designed to hold and heat a 25 x 200 mm Pyrex ignition tube which is connected to a train comprising a U-tube containing nonabsorbent cotton, a cold trap, a rotameter, an additional trap, a modified Beckman mercury vapor meter Model 23, an Erlenmeyer water trap, and a water aspirator pump.

The furnace consists of 35 feet of No. 22 Chromel A wire having a resistance of 1 ohm per foot wound on three layers of wet asbestos paper, (1/64 inch thick) around a 24-inch long, 1½ inch diameter Coors, sillimanite combustion tube with plain open ends. The windings of wire were spaced evenly at 3/32 inch apart. The ends of the wire were held temporarily in place and the windings were covered with wet asbestos cloth (1/16 inch thick, 40 inches wide) to a thickness of ¾ inch at the leads and ½ inch elsewhere, that is, the overall diameter was approximately 3 inches near the leads and 2½

These studies were supported by grants from the National Institutes of Health, Public Health Service, Department of Health, Education, and Welfare.

Presented at the Twenty-second Annual Meeting of the American Industrial Hygiene Association, Detroit, Michigan, April, 1961.

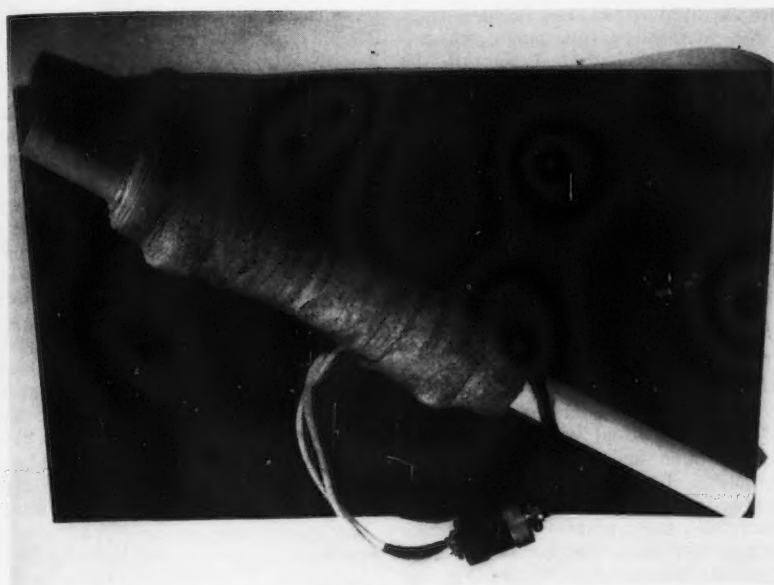


FIGURE 1. Electric furnace for mercury determination.

inches in the center and ends of the wrapping. The length of the wrapping was 12.7 inches. Two stainless-steel clamps were fastened on the ends of the asbestos cloth windings to hold the cloth firmly in place. The two wire ends were attached to these clamps. The moisture was driven off by using low heat and then the heat was increased to burn off all organic matter. The heating unit was then connected to a rheostat, (Powerstat variable transformer, type 2PF-136, 120 volts, single phase, A.C., output 2.4/2.8 KVA).

The Beckman mercury vapor meter model 23 (formerly Kruger Mercury vapor meter) was equipped with the same cell previously described.<sup>1</sup>

The glassware used in addition to the Pyrex ignition tubes consisted of 7 glass-stoppered, 16 x 150 mm, Pyrex test tubes (Corning 99650); 3-ml, Kimax volumetric flasks (Kimble 28017-A); 15-ml, micro, pear-shaped separatory funnels (Corning MW-94800); 1-ml, long-tip, Kimax measuring pipettes (Kimble 37023); and 0.1 to 0.2-ml, micro, Folin blood pipettes (Fisher 6-503-5).

#### Reagents

The reagents used were the same as those detailed in the Jacobs, Yamaguchi, Goldwater, and Gilbert<sup>1</sup> method, namely, 6% potassium permanganate solution, concentrated sulfuric acid, 6

mg. of purified diphenylthiocarbazone dissolved in a liter of pure chloroform (dithizone extraction solution), standard stock mercury solution containing 0.135 gram mercuric chloride per 100 ml of 0.25 *N* sulfuric acid equivalent to 1 mg of mercury per milliliter of solution, standard working mercury solutions of 0.1 microgram per milliliter, and 20% hydroxylamine solution. The latter, however, was prepared somewhat differently: 40 grams of  $\text{NH}_2\text{OH} \cdot \text{HCl}$  was dissolved in distilled water and made up to 200 ml. This was shaken with dithizone extraction solution a few times until the last extract was green and showed no color change from its initial color.

#### Preparation of Standard Curve

A standard curve was made each time a new dithizone extraction solution was prepared. This was done as previously detailed.<sup>1</sup> The curves obtained were virtually identical with those reported before.

#### Procedure

Transfer 0.1 ml of blood to a glass-stoppered 16 x 150 mm test tube. Place in an ice bath and add carefully 0.4 ml of concentrated sulfuric acid. Remove from ice bath and swirl gently to dissolve the blood. Warm on a water bath to 50°C. Replace in the ice bath and add cau-

tiously drop by drop with shaking between drops 3 ml of 6% potassium permanganate solution. Remove from the ice bath and place in the warm water bath for 2 minutes, remove from the warm water bath and allow to stand for 15 minutes. Add additional permanganate if necessary. Repeat the steps of warming and allowing to stand two more times for a total elapsed time of 1 hour. Make certain the mixture is cold and add 20% hydroxylamine solution drop by drop with shaking until all the potassium permanganate is decolorized and the manganese dioxide is dissolved. When the last drop is added, again make certain the tube is cool, stopper, shake vigorously, cautiously open to relieve the pressure, and allow to stand for at least 10 minutes loosely stoppered.

Transfer the contents of the test tube quantitatively to a dry 15-ml separatory funnel. Wash the tube three times with 2-ml of distilled water, stoppering the tube each time and shaking vigorously. Add the washings to the micro-separatory funnel. Add 1 ml of dithizone extraction solution and shake vigorously for one minute. Relieve the pressure by opening the mouth of the funnel and not the stopcock. Allow the phases to separate. Swirl to bring down the droplets of chloroform and rotate the funnel slowly holding it in a horizontal position to make the droplets coalesce, if necessary. Draw off the chloroform layer very carefully into the 3-ml volumetric flask. Repeat the extraction with 1 ml more of dithizone extraction solution repeating the prior step. Extract again with a third milliliter of dithizone extraction solution. Make to the mark with a few drops of chloroform. Stopper the volumetric flask and mix.

Transfer with the aid of a 1-ml, longtip pipette two aliquots of 1 ml of chloroform solution of dithizonate to each of two 25 x 200 mm ignition tubes. Place in a water bath and evaporate off the chloroform at 70-80°C. This generally takes 1 hour.

Carry a blank using 0.1 ml of distilled water through the entire procedure. Also evaporate 0.2 ml of dithizone extraction solution to check the zero.

One-half hour before the combustion step turn on the furnace and turn on the Beckman mercury vapor meter so they will come to equilibrium. (In our experiments setting the rheostat at 70-75 gave us a bright red in our furnace.) Turn on the water aspirator. Check the span of the mercury vapor meter.

Remove the tubes from the water bath and dry the outside of each tube. Check to see that all the chloroform has been evaporated. Connect the ignition tube which contained only the dithi-

zone extraction solution to the train and insert the tube into the furnace to within 1 inch of its mouth. Start a stop watch, record the starting time of the movement of the meter needle, the time of maximum deflection and the time the meter returns to zero. In the case of the zero tube there should virtually no movement of the needle.

One minute after the meter needle has returned to zero, remove the ignition tube being heated and replace it by one of the blank tubes. Repeat the steps of recording the starting time, maximum deflection, and return to zero. Repeat this with each blank and each test sample.

Average the meter reading of the test sample. Subtract the reading of the blank. Obtain the concentration in thousandths or hundredths of a microgram of mercury from the calibration curve. Multiply this value by 3 to obtain the total mercury concentration in the 0.1 ml of the blood sample. Multiply by 1000 to express the results in micrograms per 100 ml of blood.

#### Results

The 0.2 ml of dithizone extraction solution almost invariably gave a zero reading during a 2-minute heating period. The blank generally gave a meter reading of 0.002 to 0.003 with a starting time of meter movement at 20 seconds, a maximum deflection at about 30-35 seconds, and a return to zero at about 40 to 50 seconds. The bloods gave results from zero (after subtraction of the blank) for unexposed persons to concentrations of several micrograms of mercury per 100 ml for exposed persons. A complete report of our data is being prepared.

Most of our results by this method yielded values below 1  $\mu\text{g}/100$  ml of blood for unexposed persons; below 4  $\mu\text{g}$  for persons with slight exposure, and 27  $\mu\text{g}/100$  ml in one person exposed to mercury vapor.

One sample of kidney biopsy tissue weighing 1.9 mg and another weighing 0.29 mg (wet weight) were analyzed by this method. They contained 2.5 mg and 1.0 mg of mercury per 100 grams of kidney tissue respectively.

#### Discussion

The principal purpose in developing a method for the determination of mercury in small volumes of blood is to reduce the need for obtaining large volumes of blood for analysis for many persons not only object to having blood samples taken but even become ill when such samples are taken. When only a 0.1 of a milliliter is required, mercury determinations can be made routinely on blood samples taken for other de-

terminations such as blood sugar, cholesterol, and the like.

There are, however, certain reservations that one must make in interpreting results obtained with such small test specimens. As the size of the sample is reduced, the chance of getting a representative test specimen is also reduced if the mercury is not uniformly distributed in the blood. Thus at times the mercury concentration may appear to be less than it really is and at other times it may be higher than the true value.

There was a significant reason for changing the order of the addition of the reagents. We found in our experiments with other materials which contained organic mercurials that adding concentrated sulfuric acid first to the test specimen assisted in decomposing the mercury compound. This splitting action of the sulfuric acid was greatly diminished if it was added after the test sample had been diluted by water and the permanganate solution.

We found the direct addition of permanganate tablets rather than permanganate solution to be a poor manipulative step because the test solution had to be heated strongly to get the permanganate into solution.

The electric furnace we constructed was superior to the heating chamber of our initial method because it eliminated the need of turning the gas on and off, the heating was much more uniform, and the positioning of the ignition tube in the furnace was simpler.

As noted in the section on results the method can be applied almost without modification to the determination of mercury in tissues.

We are presently using this variation and the variation of the method detailed by Jacobs, Yamaguchi, Goldwater, and Gilbert for the determination of mercury in blood, urine, kidney tissue, fruits and vegetables, water, and fabrics. We are undertaking a study of the mercury

concentration of milk, meat, and other food products.

### Summary

A method for the determination of mercury in 0.1 ml of blood is detailed. Sulfuric acid is added to the blood in the cold; then permanganate solution is used to oxidize the organic matter; mercury is extracted by a chloroform solution of dithizone, and after evaporation of the chloroform, the mercury is liberated by heating the dithizonate in a furnace; the amount of mercury vapor produced is measured by an ultraviolet light mercury vapor meter. The method is applicable to the estimation of mercury in the nanogram range, that is,  $10^{-9}$  gram of mercury. The method virtually without change has been adopted for the determination of mercury in kidney biopsy material.

### Acknowledgment

The authors wish to thank Miss Jeanne Hernon for her assistance in this investigation.

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# A Rapid Analytical Method for the Determination of Beryllium in Air Samples

R. A. HISER, B.S., H. M. DONALDSON, M.S., and  
C. W. SCHWENZFEIER, B.S.

*The Brush Beryllium Company, Elmore, Ohio*

Adoption of hygienic controls for air-borne beryllium pointed up the need for a rapid analytical method for air samples. Such a method is described which consists of sample collection on Whatman #41 filter paper, ashing of the sample and subsequent conversion to beryllium fluoride. The formation of a lake with p-nitrophenylazoreinol, and comparison of the Klett reading with a standard curve gives beryllium content. (For optimum results, samples should contain from 5 to 45 micrograms of beryllium.) Interfering heavy metals are chelated with Dow's Versene "T". Copper and zinc are complexed with cyanide. The method is recommended only for air samples collected on Whatman #41 paper or equivalent.

ABOUT 1946, berylliosis was recognized as an occupational disease. Since the Atomic Energy Commission and its contractors were the principals involved at this time in working with beryllium, the Advisory Committee of the Atomic Energy Commission in 1949 set up recommended limits for the control of air-borne beryllium.<sup>1</sup> The recommendations were, that for in-plant exposures, no person should be exposed for any one day to an average concentration of more than 2 micrograms beryllium per cubic meter, and that no instantaneous exposures should exceed 25 micrograms per cubic meter. It is apparent that in applying these limits recommended by the Atomic Energy Commission Advisory Committee on a beryllium production facility that considerable interpretation was necessary. In 1956 when the Atomic Energy Commission issued invitations to bid for the construction of two beryllium facilities, this interpretation was formalized and incorporated as Appendix D in the Health and Safety section in the contract between the Brush Beryllium Company and the Atomic Energy Commission.<sup>2</sup>

The most significant difference from the Original Atomic Energy Commission Advisory Committee recommendation is that, instead of limiting each employee to an exposure of 2 micrograms beryllium per cubic meter for each day, the period of averaged exposure was extended to three months. Hence, the concept of

the Daily Weighted Average over a three month period was adopted. This means, that though inevitable accidents in processing would throw an operator over the 2 micrograms beryllium per cubic meter limit for some days, they could be balanced by days of normal operation. Also, realizing that accidents or malfunctioning of equipment would result in instantaneous exposures over 25 micrograms beryllium per cubic meter, respirator protection was permitted for exposures from 25 micrograms beryllium per cubic meter up to 100 micrograms beryllium per cubic meter. Operations over 100 micrograms per cubic meter are shut down until alterations can be made to bring them under control. However, in any case where operations must be run and exposures are over 100 micrograms per cubic meter, fresh air masks are worn.

In order to maintain a plant under Atomic Energy Commission control, it is necessary to sample each operation at such intervals as necessary to know the degree of contamination in the plant and to amass enough data to calculate the Daily Weighted Average on each operator over a three month period. Both the operator's general environment and his environment while performing operational functions must be measured for air-borne beryllium. These data go into his Daily Weighted Average by applying a time versus exposure study through his average work day over a three month period. (See Tables I and II).

Since monitoring of a plant requires taking a great number of samples, and since it is neces-

<sup>1</sup> Presented at the Twenty-second Annual Meeting of the American Industrial Hygiene Association, Detroit, Michigan, April 1961.

TABLE I

The Brush Beryllium Company  
Elmore, Ohio—Beryllium Plant

Daily Weighted Average for the Period  
October through December, 1960

Operation: Reduction Furnace Operator 2 men/shift; 3 shifts/day; 6 men/day

Operation or Operating Area	Time Per Opera. (Min.)	Opera. Per Shift	Time Per Shift (Min.) (T)	Number of Sample	Concentration μgm Be/M <sup>3</sup>			Conc. Times Total Time (T × C)
					Low	High	Ave.	
					(C)			
GA Reduction Furnace Area.....	369	1	369	29	0.2	5.5	0.8	295.2
GA Shoe Change Room.....	6	1	6	13	0.2	44.1	10.8	64.8
GA Locker Room.....	12	1	12	5	0.3	2.7	1.8	21.6
GA Cafeteria.....	30	1	30	5	0.1	4.9	1.7	51.0
GA General Plant.....	30	1	30	27	0.2	3.0	0.8	24.0
BZ Charge furnace.....	3.5	3	10.5	7	1.1	12.1	4.0	42.0
BZ Charge drums in charge cart.....	1.5	3	4.5	8	0.7	58.3	17.9	80.6
BZ Probe melt.....	0.5	15	7.5	7	0.3	9.6	5.1	38.3
BZ Pour furnace.....	2	3	6	9	1.0	5.9	3.0	18.0
BZ Put melt into transfer pot cart.....	0.5	3	1.5	9	2.0	15.9	6.7	10.1
BZ Dump melt into crusher elevator.....	3	3	9	6	0.8	4.9	2.5	22.5
BZ Chip & rake dross.....	4	3	12	8	2.0	6.7	3.2	38.4

$$\frac{(T \times C)}{T} = \frac{1.4}{T} \mu\text{gm Be/M}^3 \text{ 498 } \Sigma T$$

$$\Sigma(T \times C) 706.5$$

TABLE II

The Brush Beryllium Company  
Elmore, Ohio—Beryllium Plant

Daily Weighted Average for the Period  
October through December, 1960

Operation: Machine Shop Personnel 5 men/shift; 3 shifts/day; 15 men/day

Operation or Operating Area	Time Per Opera. (Min.)	Opera. Per Shift	Time Per Shift (Min.) (T)	Number of Sample	Concentration μgm Be/M <sup>3</sup>			Conc. Times Total Time (T × C)
					Low	High	Ave.	
					(C)			
GA Machine Shop Area.....	420	1	420	18	0.3	6.1	1.3	546.0
GA Shoe Change Room.....	6	1	6	13	0.2	44.1	10.8	64.8
GA Locker Room.....	12	1	12	5	0.3	2.7	1.8	21.6
GA Cafeteria.....	30	1	30	5	0.1	4.9	1.7	51.0
GA General Plant.....	30	1	30	27	0.2	3.0	0.8	24.0

$$\frac{(T \times C)}{T} = \frac{1.4}{T} \mu\text{gm Be/M}^3 \text{ 498 } \Sigma T$$

$$\Sigma(T \times C) 707.4$$

sary to analyze these samples rapidly so that the hygienic conditions of the plant can be known as soon as possible, analytical methods were examined to see how they could be utilized in meeting our needs.

The three methods considered were:

1. Spectrographic<sup>3, 4</sup>
2. Fluorimetric<sup>5</sup>
3. Zenia<sup>6</sup>.

Though all these methods would give reliable data, advantages of the Zenia method were apparent.

The Zenia method requires:

1. Less expensive equipment than for Spectrographic methods
2. Less time than Fluorimetric method and Fluorimetric method is more sensitive than is necessary
3. Less skilled personnel.

Hence, after considering the advantages of speed, cost and reliability, it was decided that the Zenia method best suited our needs.

### Sampling

A most important phase of monitoring for beryllium is the method of sampling. There are

many types of sampling equipment available; however, since small quantities of air-borne beryllium dust constitute the toxic agent, the method of sample collection falls most logically to collection by pumping contaminated air at a known rate through a filter medium and analyzing that which is caught on the filter. Whatman #41 filter paper was chosen as the standard filter medium, both for its uniformity and for its ability to pass fairly large quantities of air with minimal resistance.

After choosing the filter medium, the next in importance is the air pump necessary to collect the air sample. Though a number of different pumps can be used to collect an air sample, one pulling a relatively large volume of air in a short time is necessary in order to obtain enough beryllium on the sample pad for analytical work. For general area sampling, a large volume of air is not necessary since the sampler can be run long enough to obtain a large enough sample for analysis. However, for operational samples which are often of short duration, it is necessary to collect a sample in a short time which is sufficiently large for analysis. To meet these sampling requirements, the Staplex Hi Volume sampler<sup>7</sup>, which draws approximately 0.5 cubic meters of air per minute using a Whatman #41 filter paper, is satisfactory.

In sampling, extreme care must be taken to insure that the filter paper does not become contaminated. In the laboratory, the sampler heads are washed in detergent, dried and are then loaded with 10.5 centimeter Whatman #41 filter paper. These loaded heads are sealed in cellophane bags until ready to be placed on the sampler. After sampling, the head is carefully removed, the filter paper is removed with tweezers and placed in a new cellophane bag. These bags are enclosed in a manila envelope for transport to the laboratory. It should be noted that sample heads are used only once between detergent washes.

#### Discussion of Analytical Procedure

For most accurate results by the Zenia method, the amount of beryllium collected for analysis should be no less than 5 micrograms and no more than 45.0 micrograms. It should also be understood that this method is designed for and should be limited to in-plant samples collected on #41 Whatman filter paper or equivalent where the amount of particulate matter collected, consisting essentially of traces of iron, silica, and carbonaceous material, is small when compared to beryllium. Air samples collected on fluted pads, water samples, urine samples or others containing traces of beryllium with large

ratios of other material when compared to beryllium are not suitable for analysis by the method.

In general, the analysis of beryllium containing air samples collected on Whatman #41 filter paper involves:

1. Destruction of organic material by ignition
2. Solubilization of the beryllium
3. Complexing or removal of interfering elements
4. Colorimetric evaluation of the beryllium present.

The final evaluation of beryllium in the sample is accomplished by measuring the intensity of the lake formed with p-nitrophenylazoarcinol in alkaline solution. The adsorption of light by this colored complex does not strictly follow Beer's Law, but by controlling alkalinity, complexing of interfering elements and controlling chemical concentration, the relationship of light adsorption may be measured with a spectrophotometer, at wave length of 500 millimicrons, or a filter type photometer, such as a Klett, with a #54 (500-575 millimicron, green) filter gives good results. The Klett is used in the authors' laboratory.

Any ion which yields a color in alkaline solution will cause interference.<sup>8</sup> These are in general rendered inactive through the formation of soluble complexes. Iron and other heavy metals are complexed with Dow's Versene "T". Cyanide treatment complexes copper and zinc. Magnesium<sup>9</sup> and chloride ions should be absent since they interfere.

#### Reagents

##### 1. Standard beryllium solution:

Dissolve enough beryllium powder of known assay in a small quantity of 1:1 H<sub>2</sub>SO<sub>4</sub> so that when made up to one liter, the strength will be 1 ml equals 100 micrograms. After initial reaction between beryllium and the acid, it is usually necessary to boil the liquid to get all beryllium into solution. Standard solutions can be aliquoted as necessary for making up standards necessary to plot curve of Klett reading versus micrograms of beryllium.

##### 2. Buffer solution:

78 grams NaOH  
31.5 grams Citric Acid  
18.5 grams Boric Acid  
Make up to one liter in volumetric flask.

##### 3. p-Nitrophenylazoarcinol (Zenia) solution:

Dissolve 0.25 grams of dye in 1.0 liter of 0.1 N NaOH. Stir in darkness for at least five hours,

using magnetic stirrer, or equivalent, then filter under vacuum. Allowing this solution to stand for eight hours in darkness and refiltering tends to stabilize the resultant standardization curve. This reagent is not uniform, a new standardization curve must be plotted for each lot of dye made up. (The dye is available from Eastman Kodak, Catalog List No. 41 as No. P4414-4-(p-nitrophenylazo)orcinol.)

#### 4. Versene "T" reagent:

Dilute 1 part of Dow's Versene "T" (55.5% solids) as received with 1 part distilled water.

#### Analytical Procedure

Remove filter paper containing sample from cellophane bag and place in platinum dish (bag and filter paper can be ignited, but experience has shown that all beryllium is impinged on filter paper and bag will not contain a significant quantity of beryllium). Wet with 1:1  $H_2SO_4$  from a dropping bottle. Evaporate on hot plate to fumes, then place on gas burner, increasing heat slowly until sample is thoroughly ashed. Cool platinum dish, wet with  $HNO_3$  (dropping bottle), place on cool portion of hot plate to evaporate, then repeat firing. Again cool platinum dish, add about 10 drops of HF and swirl dish to dissolve the ash, evaporate to dryness at low heat. (Caution: Do not allow hot plate surface to exceed  $200^\circ F$ !) Dissolve residue in platinum with a few milliliters of cold water.

Add 1 drop of Versene "T" reagent. (Solution should be alkaline to litmus at this point, if not, adjust with a few drops of 1 N NaOH.) If copper is present, as indicated by blue color, or zinc is suspected, add KCN solution until color disappears. Then add 1.0 ml of buffer solution, transfer into cuvette tube, taking care to leave room in cuvette for 1.0 ml of Zenia (dye). Add 1.0 ml of dye, make up to 10 ml with distilled water. Mix by stopping cuvette with finger and upending tube. Centrifuge for 10 minutes. Place cuvette in Klett and read, the instrument having been zeroed with a reagent blank containing exactly the same amount of Versene Reagent, buffer and dye.

Read the amount of beryllium from previously prepared plot of instrument reading versus micrograms of beryllium. (Figure 1.) Usually 20 or more samples are read at the same time. The zero reading should be checked before and after each set of samples. Along with samples, a known standard should be prepared and read to make certain that the prepared curve remains valid.

Samples in excess of 45.0 micrograms of beryllium must be aliquoted since accuracy falls off at this point.

#### Recovery of Beryllium from Known Samples Deposited on Whatman #41 Filter Paper

To evaluate the accuracy of our method, a series of "Spiked" samples were prepared by titrating known amounts of a standard beryllium

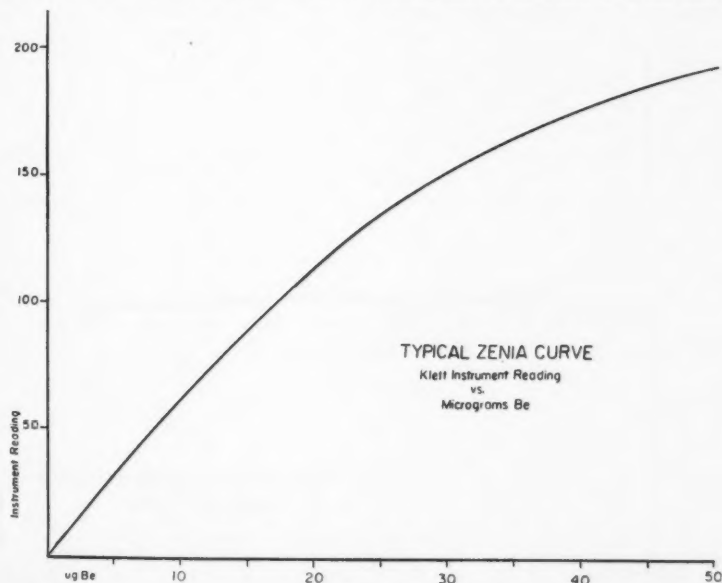


FIGURE 1.

sulfate solution on filter paper and allowing these to dry in a beryllium free atmosphere. These samples were run along with our regular analytical program by semi-skilled laboratory personnel and were treated in the same manner as any air sample taken in the plant. Spiked samples contained amounts of beryllium ranging from 2.5 micrograms up to 45.0 micrograms. The

results of these analyses are tabulated in Table III.

A plot of the amount of beryllium recovered at various levels shows per cent recovery in the 2.5 micrograms samples was 118%, whereas samples over 5 micrograms thru 45 micrograms showed recovery near 100%. Data are shown in Table III and plotted in Figure 2.

TABLE III  
Analytical Data—Zenith Method

Amount of Beryllium ( $\gamma$ ) Present.....	2.5	5.0	7.5	10.0	15.0	20.0	22.5	25.0	30.0	37.5	40.0	45.0
2.4	6.0	6.4	8.9	16.7	17.4	22.5	25.0	30.4	37.1	40.5	44.1	
2.3	4.8	7.2	10.0	14.0	20.0	23.4	24.3	30.0	37.0	39.2	44.6	
3.2	4.4	6.2	9.1	15.0	17.8	22.3	24.3	30.0	37.0	39.6	42.9	
2.6	6.1	8.3	9.6	14.3	18.6	23.6	25.0	28.6	34.3	38.9	44.0	
2.2	5.4	6.8	9.8	16.0	19.0	23.0	27.0	30.0	37.0	40.6	43.8	
1.5	5.7	6.5	10.0	15.1	18.0	22.4	26.7	28.1	37.6	39.6	43.9	
3.1	5.6	7.4	10.7	14.8	20.7	22.0	27.7	31.0	36.6	43.8	45.7	
2.2	5.0	8.1	9.3	15.2	23.0	22.4	24.3	30.6	37.2	38.2	44.5	
3.9	4.7	7.8	9.8	15.0	20.2	22.5	24.5	30.5	40.0	38.9	45.4	
Amount of Beryllium ( $\gamma$ ) Recovered.....	3.9	6.2	9.3	11.8	14.6	20.8	22.7	24.8	30.9	36.5	42.7	50.7
2.1	5.2	7.0	11.2	15.4	18.6	23.0	27.7	28.8	37.1	40.0	43.8	
3.1	4.0	8.0	10.6	14.8	20.0	22.8	26.7	29.6	37.5	37.7	44.0	
3.4	6.4	7.7	11.2	15.0	21.7	21.8	25.0	27.7	38.1	33.2	43.8	
3.3	4.2	7.3	7.7	15.2	20.8	21.8	26.7	30.0	37.1	32.6	46.8	
3.6	5.2	7.9	10.4	15.1	21.4	21.7	24.2	30.0	37.2	36.2	46.8	
3.4	5.4	8.8	9.1	15.0	21.1	22.2	26.1	29.8	36.8	38.5	47.8	
3.1	5.0	7.0	10.9	14.6	19.8	22.5	23.9	29.0	37.1	36.2	44.4	
3.6	5.2	8.2	10.2	17.2	18.3	22.2	24.5	30.1	37.0	39.2	44.1	
2.5	6.1	6.4	10.0	15.7	18.5	22.5	27.8	30.9	39.9	39.6	43.0	
3.6	4.8	10.0	10.7	15.0	22.5	23.0	26.7	33.0	37.4	41.8	43.3	
Average Recovery of Beryllium ( $\gamma$ ).....	3.0	5.3	7.6	10.1	15.2	19.9	22.5	25.7	30.0	37.3	38.9	44.9

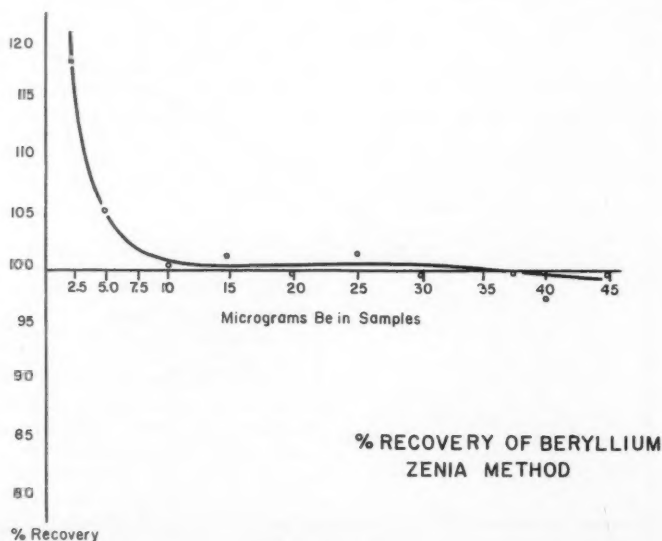


FIGURE 2.



A frequency distribution of the per cent recovery of these samples plots a standard curve over the range 5.0 micrograms thru 45.0 micrograms and shows a standard deviation of 8.4%. This means a 68% confidence level of  $\pm 8.4\%$  from the true value or a 95% confidence level of  $\pm 16.8\%$ . To put it in a different way, 68% of the values will fall within  $\pm 8.4\%$  of the true value or 95% will fall within the range of  $\pm 16.8\%$  of the true value. This degree of accuracy is sufficient for this type of air sample work.

### Summary and Conclusion

The need for and development of a rapid analytical method for the analysis of beryllium in air samples has been described. This method, the so-called Zenia Method, consists of the addition of p-nitrophenylazoarcinol to a prepared beryllium sample. The reading of the adsorption of the resulting color on a Klett, using a #54 (500-575 millimicron, green) filter and comparing with a standard curve, gives a measure of the amount of beryllium in the sample. It must be remembered that this method is limited to in-plant sampling where sample collection is attained with Whatman #41 filter paper or equivalent. Any element that forms a color in alkaline

solution will interfere; however, many interfering constituents like heavy metals may be chelated with Versene "T" or complexed with cyanide. The presence of magnesium and chloride interfere with the method. Samples containing between 5 and 45 micrograms beryllium show a standard deviation of 8.4% and a 68% confidence level for values between  $\pm 8.4\%$  of true value or 95% confidence level for values falling within  $\pm 16.8\%$  of the true value. Such analytical accuracy is adequate for the in-plant monitoring of a beryllium facility.

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### 1962 ANNUAL MEETING OF AIHA

THE 1962 ANNUAL MEETING of the American Industrial Hygiene Association will be held in Washington, D. C., at the Park-Sheraton Hotel, May 13-17. Please make a special note of the time and place of this meeting and make your plans to contribute to the program and to attend the meeting. You may recall that the meeting was originally scheduled for Baltimore, Maryland; however, the notable success of the 1961 meeting in Detroit made it apparent that the facilities which were available in Baltimore would not be adequate for our needs. The committee made a quick but careful survey of the situation and was fortunate to be able to make the present arrangements to meet in Washington. We shall be expecting to see you there.

# Studies on the Analysis of Hydrocarbons from Incinerator Effluents with a Combustible Gas Indicator

MILTON FELDSTEIN

*Bay Area Air Pollution Control District, 1480 Mission Street,  
San Francisco 3, California*

A combustible gas indicator with a 10 to 1 sensitivity scale has been found to be applicable to the measurements of  $C_2$  and higher hydrocarbons from incinerator effluents. Samples are collected in evacuated stainless steel 34-liter tanks. Response to carbon monoxide and methane was differentiated from higher hydrocarbons through the difference in indication with and without a tube of activated carbon in the sampling train. The method is applicable to differentiate between incinerators emitting less than 50 ppm total hydrocarbons and those emitting higher concentrations.

**P**ERFORMANCE standards for hydrocarbon emissions from incinerators have been adopted by the Bay Area Air Pollution Control District.<sup>1</sup> The emission limit has been set at 50 ppm (volume) or less of  $C_2$  through  $C_6$  hydrocarbons. The regulation also provides that the primary method for the measurement of these hydrocarbons shall be by gas chromatography. The gas chromatograph provides an accurate and sensitive method for the measurement of hydrocarbons, and in addition, it permits the separation of the hydrocarbon mixture into its components. However, the method is time-consuming and requires fairly skilled persons for the operation and interpretation of data obtained. In an effort to simplify the procedure, a study was begun on the use of a combustible gas indicator to measure the concentration of hydrocarbons in incinerator effluents.

Combustible gas indicators were designed to measure the lower explosive limit of gases, or mixtures of gases, in confined places. They have been used to measure the concentration of gases in tunnels or sewers to determine whether or not an explosion hazard was present. Most of the lower explosive limits (LEL) of the common gases measured are in the 1-2% range. This concentration is much too high in terms of the emission standard for incinerator effluents. However, some of the commercial instruments available have a 10 to 1 sensitivity range which increases

the sensitivity 10 times, thus making it possible to measure certain gases in the part per million range. The instrument which was used in this study was a Davis Model M6, Type L, Combustible Gas Indicator, with a 10 to 1 sensitivity scale.

Combustible gas indicators utilize the principle that electrical resistance in a given metal wire is a function of the temperature of the wire. As shown in the schematic diagram (Figure 1), the atmosphere to be tested is drawn across a heated catalytic filament. This filament forms one leg of a wheatstone bridge which has been previously balanced in an atmosphere containing no combustible material. The combustion of the sample in the analyzing chamber raises the temperature and, therefore, the electrical resistance of the filament. The resultant unbalance in the wheatstone bridge circuit causes a current to flow. The current is measured and is a function of the concentration of combustible material present.

The instrument is calibrated by drawing mixtures of known concentrations of specific hydrocarbons through the sampling side. Figure 2 shows the calibration curves obtained with a series of hydrocarbons in the part per million range. The instrument was used with the high (10 to 1) sensitivity range for these calibration runs.

In operation a sample of the gas to be analyzed is drawn through the chamber containing the heated platinum filament by means of a rubber aspirator bulb. The sample passes

<sup>1</sup>Presented at the Twenty-second Annual Meeting of the American Industrial Hygiene Association, Detroit, Michigan, April 1961.

through a drying compartment containing calcium chloride to remove moisture. The response of the meter is noted, and by reference to proper calibration tables, the concentration of hydrocarbon is recorded.

At the outset three problems were recognized in the application of the instrument to the measurement of hydrocarbons present in incinerator effluents. These are as follows:

(1) Carbon dioxide causes a negative response in the electrical system, presumably by removing heat from the platinum filament, and thus changing its resistance. Inasmuch as there are generally large quantities of  $\text{CO}_2$  present in incinerator effluents (2-12 per cent), it was necessary to remove  $\text{CO}_2$  from the sample stream.

(2) Carbon monoxide is burned at the platinum filament in a manner similar to hydrocarbon combustion; however, the heat production and hence the response is less than with an equivalent concentration of hydrocarbon. Inasmuch as large amounts of carbon monoxide are generally present in incinerator effluents, it was necessary to study the removal of carbon monoxide from the sample stream.

(3) The emission limits for hydrocarbons prescribed by the regulation include only  $\text{C}_2$  through  $\text{C}_6$  hydrocarbons, excluding methane from regulation. Inasmuch as methane is generally a relatively large component of the gases emanating from incinerator effluents, it was necessary to study the possible removal of this gas from the sample stream.

### Sampling Procedure

It has been shown<sup>2</sup> that the concentration of hydrocarbons emitted from an incinerator stack varies markedly, apparently depending on the charging rate, the quantity of excess air and the stoking rate. Hydrocarbon concentration can vary from 0 to 600 ppm in as little as 1.5 to 2.0 minutes. Since these concentrations vary quite widely, it was deemed necessary to collect an integrated sample of effluent. This was accomplished by collecting samples in evacuated stainless steel tanks over a 15-minute period.<sup>3</sup> All analytical data reported here was done on such integrated samples collected in the field.

### Removal of Carbon Dioxide

In order to remove carbon dioxide from the sample stream the calcium chloride drying agent in the drying chamber of the instrument was replaced with ascarite. Analyses were made with

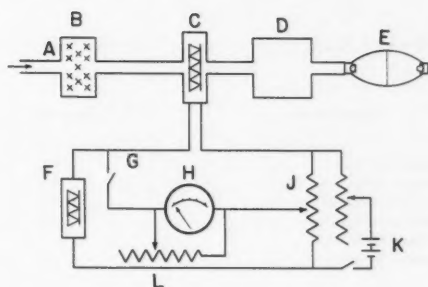


FIGURE 1. Schematic diagram of a combustible gas indicator.

- A—Air enters
- B—Drying agent
- C—Detector filament
- D—Tank
- E—Aspirator bulb
- F—Reference filament
- G—Switch
- H—Meter
- J—Zero adjust
- K—Dry cells
- L—Calibration control

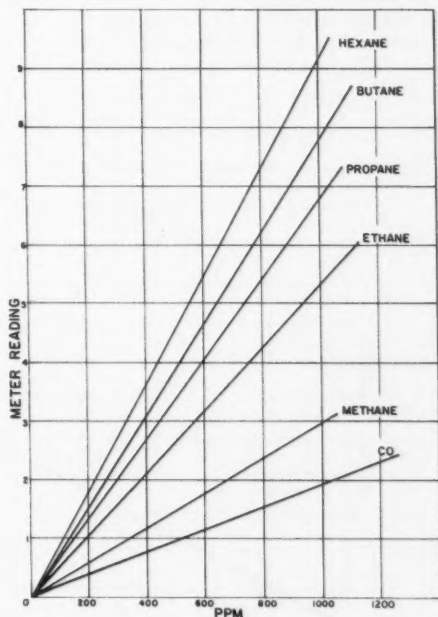


FIGURE 2. Calibration curve—Combustible gas indicator.

TABLE I  
Effect of Ascarite on Combustible Gas Indicator Response

Hydrocarbon	Carbon Dioxide %	Meter Reading
Ethane 100 ppm.....	0	0.5
Ethane 100 ppm.....	2	0.5
Propane 400 ppm.....	0	2.2
Propane 400 ppm.....	4	2.2
Butane 500 ppm.....	0	3.8
Butane 500 ppm.....	6	3.8
—	2	0
—	4	0
—	6	0

known concentrations of hydrocarbons with and without varying concentrations of carbon dioxide. The results of these tests are shown in Table I, and they indicate that ascarite effectively removes carbon dioxide, but does not affect the response of the instrument to hydrocarbons.

#### Removal of Carbon Monoxide

A series of absorbing materials were tested for their efficiency in removing carbon monoxide or hydrocarbons from a sample stream containing known mixtures of both compounds. The tests were accomplished as follows: A  $\frac{1}{4}$ " x 6, 12 or

18" glass tube was packed with the absorbent under study. This tube was placed in a sample line and the known mixture of carbon monoxide and hydrocarbons was allowed to pass through the column before entering the analyzing chamber of the instrument. The response was noted and compared to a reading obtained by the same sample without the absorbing column in the line. Table II and Figure 3 show the results of these

TABLE II  
Effect on Hydrocarbons and Carbon Monoxide by Activated Carbon Column

Hydrocarbon	ppm	Carbon Monoxide (ppm)	Meter Reading	
			(with carbon)	(without carbon)
Methane.....	100	0	0.3	0.3
Methane.....	200	0	0.7	0.7
Methane.....	0	1000	1.6	1.6
Methane.....	200	1000	2.4	2.4
Butane.....	100	0	0	0.9
Butane.....	100	1000	1.6	2.5
Propane.....	200	0	0	1.3
Propane.....	200	1000	1.6	2.8
Ethane.....	400	0	0	2.1
Ethane.....	400	1000	1.6	3.7
—	—	2000	3.1	3.1
—	—	4000	6.2	6.2
—	—	5000	7.8	7.8

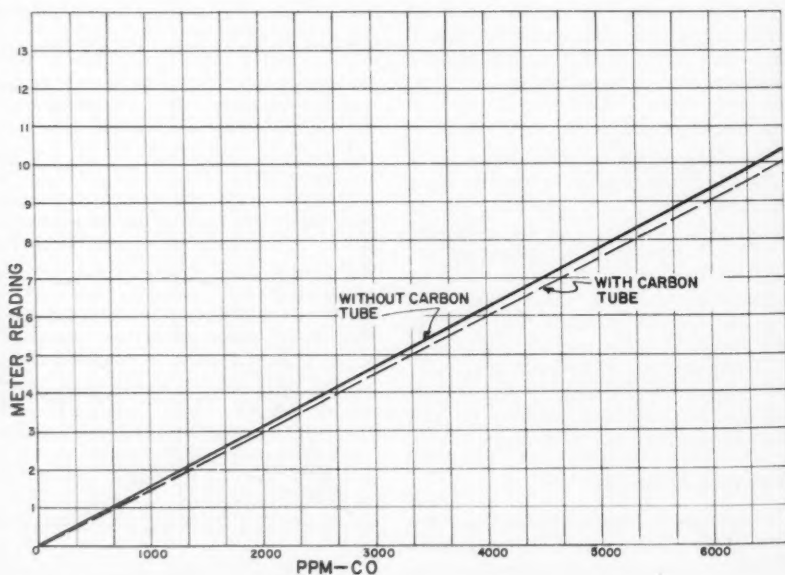


FIGURE 3. Effect of carbon adsorption tube on carbon monoxide response.

through a drying compartment containing calcium chloride to remove moisture. The response of the meter is noted, and by reference to proper calibration tables, the concentration of hydrocarbon is recorded.

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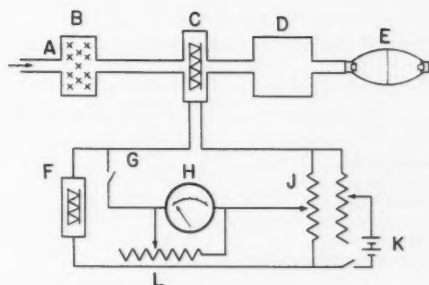


FIGURE 1. Schematic diagram of a combustible gas indicator.

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- F—Reference filament
- G—Switch
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- L—Calibration control

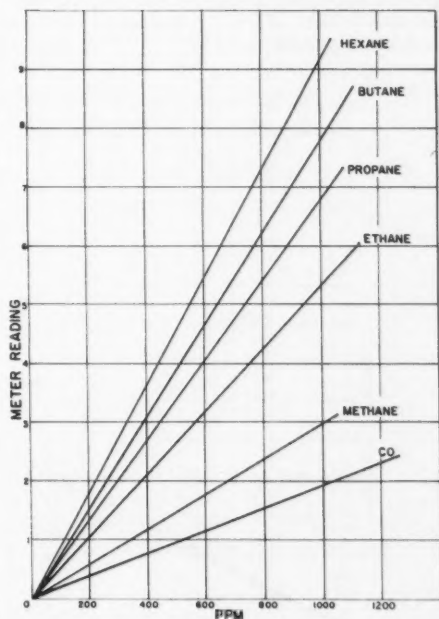


FIGURE 2. Calibration curve—Combustible gas indicator.



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Butane 500 ppm.....	0	3.8
Butane 500 ppm.....	6	3.8
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—	4	0
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18" glass tube was packed with the absorbent under study. This tube was placed in a sample line and the known mixture of carbon monoxide and hydrocarbons was allowed to pass through the column before entering the analyzing chamber of the instrument. The response was noted and compared to a reading obtained by the same sample without the absorbing column in the line. Table II and Figure 3 show the results of these

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Methane.....	200	1000	2.4	2.4
Butane.....	100	0	0	0.9
Butane.....	100	1000	1.6	2.5
Propane.....	200	0	0	1.3
Propane.....	200	1000	1.6	2.8
Ethane.....	400	0	0	2.1
Ethane.....	400	1000	1.6	3.7
—	—	2000	3.1	3.1
—	—	4000	6.2	6.2
—	—	5000	7.8	7.8

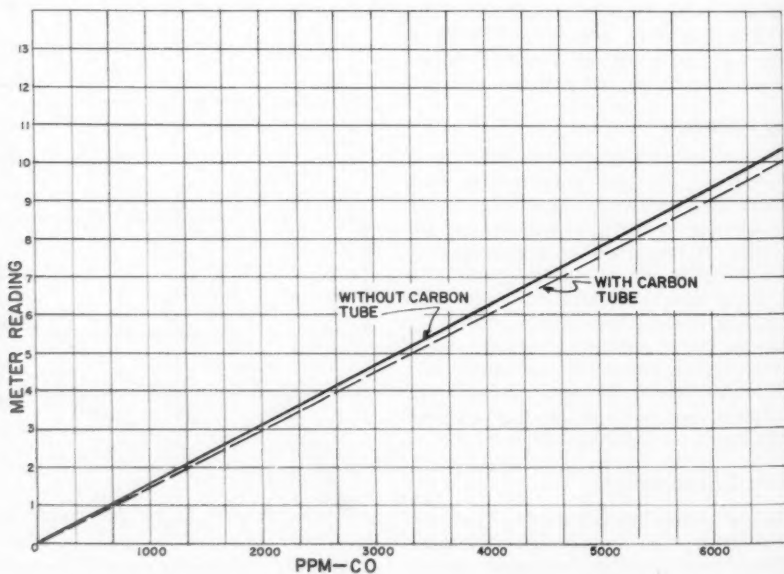


FIGURE 3. Effect of carbon adsorption tube on carbon monoxide response.

tests using Pittsburgh activated carbon Type BPL, 60-80 mesh in a 1/4" x 8" tube. The data indicate that an activated carbon column effectively removes C<sub>2</sub> and higher hydrocarbons but does not remove carbon monoxide. Thus, with a given sample, if readings were taken first without a carbon tube in the sample line, and then with a carbon tube in the line, the difference in the readings is a measure of the hydrocarbon content of the sample.

### Separation of Methane

Because of the restriction imposed on the measurement of hydrocarbons to exclude methane, it was necessary to study the effect of the absorbing materials used on the separation of this compound from C<sub>2</sub> and higher hydrocarbons. Reference is made to Table II where it is shown that methane, along with carbon monoxide, passes rapidly through the activated carbon column, whereas C<sub>2</sub> and higher hydrocarbons are selectively retained on the column. Thus the difference in reading obtained with the combustible gas indicator, with and without a carbon column, reflects the concentration of C<sub>2</sub> and higher hydrocarbons. The rapid and relatively complete passage of methane through the carbon column is also shown in Figure 4 where readings on known concentrations of methane are compared in tests with and without a carbon column.

### Effect of Tank Pressure on Response of Combustible Gas Indicator

During the analysis of incinerator effluents obtained in 34-liter tanks it was found that the meter response began to increase as the vacuum increased within the tank. However, it was noted that a vacuum of less than 100 mm of Hg had no effect on the reading. It was necessary, therefore, to take readings on the sample before the vacuum in the tank reached this point. This was readily accomplished by limiting the sampling time for each analysis (with and without carbon tube) to 30 seconds. At the end of a full minute of sampling the vacuum developed within the tank was insufficient to affect the meter reading. The data is shown in Table III.

### Effect of Flow Rate on Meter Reading

During the testing procedure it became apparent that the rubber aspirator bulb did not provide a steady stream of sample through the instrument. A small diaphragm pump was substituted for the rubber bulb, and studies were made to determine the effect of flow rate on

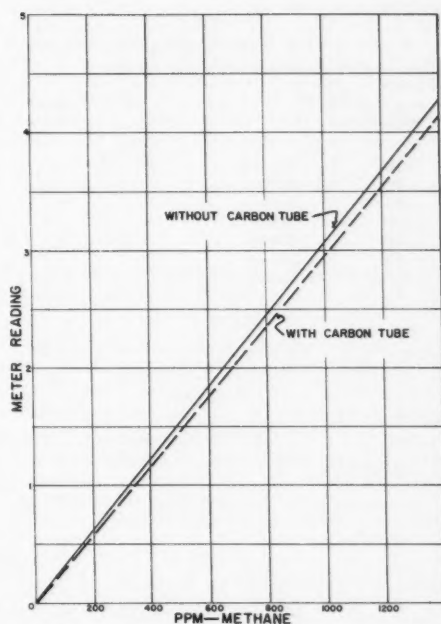


FIGURE 4. Effect of carbon adsorption tube on methane response.

TABLE III

Effect of Vacuum on Meter Reading in the Presence of Hydrocarbons

Pressure (mm Hg)	Hydrocarbon (100 ppm)	Meter Reading
760	Methane	0.3
700	Methane	0.3
660	Methane	0.3
600	Methane	0.6
500	Methane	1.5
760	Butane	0.9
660	Butane	0.9
500	Butane	1.9
760	Ethane	0.5
660	Ethane	0.5
500	Ethane	1.7

meter response. These data are shown in Table IV. The data indicates that a flow rate of 100 to 200 cc per minute is adequate to obtain a steady response in the presence of hydrocarbons.

### Procedure for Analysis

The procedure which was adopted for the measurement of C<sub>2</sub> and higher hydrocarbons from incinerator effluents is as follows:

TABLE IV  
Effect of Flow Rate on Meter Reading of  
Combustible Gas Indicator

Flow Rate (ml/min.)	Hydrocarbon	ppm	Meter Reading
100	Methane	100	0.3
200	Methane	100	0.3
400	Methane	100	0.5
100	Butane	100	0.8
200	Butane	100	0.8
400	Butane	100	0.9

TABLE V  
Comparison of Results of Incinerator Analysis by  
Gas Chromatography and Combustible  
Gas Indicator

Sample No.	C <sub>2</sub> and higher hydrocarbons (ppm)	
	Gas Chroma- tography	Combustible Gas Ind.
1	42	50
2	250	230
3	5	0
4	20	40
5	750	710
6	55	60
7	125	120
8	12	0
9	8	0
10	430	400

1) Sample is collected in an evacuated stainless steel 34-liter tank over a 15-minute period.

2) Ascariite was substituted for the calcium chloride drying agent in the instrument.

3) A small diaphragm pump and limiting orifice to control the flow at 100-200 cc per minute was substituted for the rubber aspirator bulb on the instrument.

4) The sampling line was connected to the 34-liter tank, and sample was permitted to flow through the instrument for a period of 30 seconds. A reading was taken at the end of this period. This reading is proportional to the total combustible content of the sample.

5) The carbon adsorption tube was inserted in the sample line, and again sample was permitted to flow through the instrument for a period of 30 seconds. A reading was taken at the end of that time. This reading is proportional to carbon monoxide plus methane concentration.

6) The difference in the readings is proportional to the concentration of C<sub>2</sub> and higher hydrocarbons present in the sample.

### Calibration

Results were expressed as parts per million propane. Reference to Figure 2 indicates that propane is intermediate in response between ethane and butane. Infrared and gas chromatographic studies<sup>3,4</sup> have indicated that the major portion of hydrocarbons present in incinerator effluents consists of methane plus C<sub>2</sub> and C<sub>3</sub> hydrocarbons, and that the C<sub>4</sub> hydrocarbons are present in relatively low concentrations.

### Comparison with Gas Chromatographic Analysis

Incinerators of good design which emitted less than 50 ppm total C<sub>2</sub> to C<sub>6</sub> hydrocarbons showed relatively little response with the combustible gas indicator. Those incinerators of poor design which emitted large concentrations of hydrocarbons showed a relatively large response with the combustible gas indicator. Table V compares the results of analyses on samples by gas chromatography and combustible gas indicator. It can be seen from the table that the instrument can be used to differentiate between incinerators emitting less than 50 ppm total C<sub>2</sub> through C<sub>6</sub> hydrocarbons, and those which are emitting large quantities of hydrocarbons.

### Summary

A combustible gas indicator with a 10 to 1 sensitivity scale has been studied in relation to the measurement of C<sub>2</sub> and higher hydrocarbons from incinerator effluents. Incinerator effluent samples are collected in evacuated stainless steel 34-liter tanks, and the integrated samples analyzed with the combustible gas indicator. The instrument was modified in that the drying agent was replaced with ascariite, and a small diaphragm pump was substituted for the rubber aspirator bulb. Response to carbon monoxide and hydrocarbons was differentiated by means of a tube of activated carbon which adsorbed hydrocarbons, but did not adsorb carbon monoxide or methane. The instrument can be used to differentiate between incinerators emitting less than 50 ppm total hydrocarbons, and those emitting higher concentrations of hydrocarbons. Precautions to be observed in the use of the instrument for the measurement of C<sub>2</sub> and higher hydrocarbons are discussed.

### Acknowledgment

The author wishes to acknowledge the helpful comments and suggestions from John E. Yocom,

Director of Technical Services, Bay Area Air Pollution Control District, San Francisco, California.

### References

1. Regulation 2, Bay Area Air Pollution Control District, San Francisco, California. May 4, 1960.
2. ROSE, A. H., ET AL.: Air Pollution Effects of Incineration Firing Practices and Combustion Air Distribution. *J. Air Poll. Control Assoc.* 8: 279 (1959).
3. FELDSTEIN, M., ET AL.: Collection and Infrared Analysis of Low Molecular Weight Hydrocarbons from Combustion Effluents. *Am. Ind. Hyg. Assoc. J.* 20: 374 (1959).
4. TUTTLE, W. N., AND M. FELDSTEIN: Gas Chromatographic Analysis of Incinerator Effluents. *J. Air Poll. Control Assoc.* 10: 427 (1960).

### PAPERS FOR THE 1962 MEETING

THE TWENTY-THIRD ANNUAL MEETING of the American Industrial Hygiene Association will be held at the Park-Sheraton Hotel, Washington, D. C., May 13-17, 1962. The Program Committee is already at work and persons interested in offering papers should notify the Program Chairman or the appropriate Session Arranger as soon as possible. Selection of papers to be accepted will be made in October, 1961. Authors of papers which are accepted will be notified of requirements and facilities. An abstract of each paper is desired by January 1 and required by February 1, 1962. In keeping with AIHA policy, the AIHA Journal will have first rights of publication of all papers presented and the decisions regarding requests for release shall be the prerogative of the Journal.

Following are the names and addresses of the Program Chairman and the Session Arrangers:

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General Electric Company  
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Nuclear Division  
Combustion Engineering, Inc.  
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Liberty Mutual Insurance Co.  
175 Berkeley Street  
Boston 17, Massachusetts

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407 Grant Street  
Wausau, Wisconsin

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2422 Afton Place  
Lansing 6, Michigan

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5602 Woodmont Avenue  
Baltimore 12, Maryland

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Supervisor, Ind. Safety Section  
Central Office Bldg., Room 287  
Ford Motor Company  
Dearborn, Michigan

#### Medical

Dr. Dave Fassett  
Eastman Kodak Company  
Kodak Park Works  
Rochester 4, New York

# Determination of Arsenic in Air and Biological Materials

L. DUBOIS and J. L. MONKMAN

*Department of National Health and Welfare, Ottawa, Canada*

A comparative study of three widely used methods for the determination of arsenic in air and biological materials was undertaken. The Gutzeit method, the silver diethyl dithiocarbamate method, and an iodine microtitration with electrical indication of the endpoint were studied. On the basis of this investigation it is concluded that the silver diethyl dithiocarbamate method is superior to the others when all factors are considered.

IN THIS laboratory, over a ten year period, a large amount of analytical data has been accumulated on arsenic. Regular analyses of arsenic-containing smelter effluents and associated biological samples have been carried out by three separate methods. While retaining the usual analytical requirements of accuracy, sensitivity and specificity, techniques and apparatus were modified as necessary to achieve the maximum number of analyses per day. Using some of this data, the relative merits of the three methods are discussed.

## Method No. 1

This method, associated with the name Gutzeit, was essentially as given in the AOAC *Methods of Analysis*<sup>1</sup> with some modifications. No rubber connections were used, the glass apparatus consisted of the usual generator bottle, absorber and indicator tube connected by ground joints. This combination of glassware may be used for water samples and previously prepared digests, alternatively, the generator bottle may be substituted by a 125 ml Erlenmeyer flask. A biological sample (urine, vegetation, etc.) may be measured into the flask, digested, and Gutzeit generation carried out without transfer and possible loss. Hydrochloric acid is the acid of choice except for biological digests. In this case it is convenient to use the residue of concentrated sulphuric acid as the source of acid. Neutralization of the sulphuric acid so that hydrochloric acid may be used, complicates the analysis unnecessarily, with, at the same time, danger of increasing the blank value. The Gutzeit assemblies are placed in a large tray containing water and ice (temp. 10-

15°C). The samples are cooled down to this temperature before gas evolution is started, and are maintained at 20°C or less during the complete course of the run. The purpose of this is twofold, to prevent the possible formation of large amounts of hydrogen sulfide if a sulfuric digest should become too warm, and to minimize the stretching of stains which may result if hydrogen evolution is too rapid. As the paper strips are supplied in groups of 16, a run consists of 16 or 32 samples run simultaneously, of which at least one is a blank, and six are standards. With sufficient glassware one analyst can handle 64 or more determinations, including standards, per day. We found the use of sand in the sulfide absorber to be a messy and uncertain procedure. Other expedients were tried, including a lead acetate-glass wool plug, and similarly impregnated dental dams. These were used both wet and dry. The most convenient procedure, however, was found to be the use of perforated glass beads previously soaked in lead acetate solution and dried. These beads were efficient as absorbers, did not restrict gas flow, and it was easy to see when replacement was required. As the internal diameter of commercially available indicator tubes was found to vary between 2.0 to 6.0 mm we prepared our own by sealing the necessary length of carefully measured borosilicate tubes to male joints. Uniformity of bore was between 2.1-2.4 mm.

## Method No. 2

This was the method originally introduced by Vasak and Sedivec<sup>2</sup> as modified and adopted by the ACGIH.<sup>3</sup> The glassware described is now available from Fisher Scientific Co. It consists of three pieces, the flask and absorber being similar to those used for Gutzeit analyses. The third

Presented at the Twenty-second Annual Meeting of the American Industrial Hygiene Association, Detroit, Michigan, April, 1961.



component is a receiver to hold absorbing reagent. Again the Erlenmeyer flasks may be used directly for biological sample preparation. We do not believe more complicated receivers to be necessary for the quantitative collection of arsine. The reagent used, the silver salt of diethyl dithiocarbamic acid, is now available from Eastman Organic Chemicals Department and Fisher Scientific Company.

The absolute accuracy of this method was evaluated for the ACGIH in 1955 as follows. Four arsenic standards were prepared and distributed to 7 collaborating analysts. The composition of the standards, known only to the referee, were, in parts per million:

Sample	Arsenic added	Antimony added
1	0.05	Nil
2	0.50	Nil
3	1.00	0.5
4	1.50	Nil

TABLE I

Analyst	Arsenic Found			
	1	2	3	4
1	0.06	0.50	1.04	1.50
2	0.043	0.49	1.02	1.38
3	0.047	0.52	1.08	1.47
4	—	0.47	0.88	1.52
5	0.05	0.49	1.02	1.49
6	0.046	0.46	0.98	1.40
7	0.043	0.48	0.86	1.56
8	0.049	0.51	1.05	1.62

TABLE II

Comparison of Analytical Methods  
(arsenic in water samples)

No.	Gutzeit		Silver Salt		Iodine	
1.	1.8	2.07	1.78	1.96	2.8	2.50
2.	2.5	2.80	2.38	1.96	3.49	2.76
3.	2.3	2.74	2.32	2.68	3.35	2.12
4.	0.037	0.052	0.008	—	0.43	0.52
5.	27.5	28.4	29.2	—	16.5	18.5
6.	0.25	0.257	0.22	0.23	0.47	0.43
7.	0.067	0.077	0.02	0.025	0.24	0.30
8.	0.082	—	0.02	0.025	0.3	0.30
9.	0.06	0.077	0.02	0.02	0.52	0.56
10.	0.83	0.87	0.63	0.68	1.72	1.22
11.	0.73	0.82	0.67	0.73	0.92	0.82
12.	0.067	0.07	0.022	0.025	0.30	0.30
13.	0.55	0.77	—	0.33	0.80	0.75
14.	1.32	1.53	1.1	1.24	1.5	1.46
15.	3.88	4.47	4.53	4.90	3.21	3.69
16.	3.24	3.06	3.63	3.66	2.89	3.32
17.	0.76	0.90	0.65	0.73	1.10	1.12
18.	0.087	0.112	0.037	0.37	0.33	0.41
19.	3.37	4.00	4.	3.65	1.89	2.57
21.	0.087	0.087	0.017	0.17	0.33	0.32

TABLE III  
Water Samples

	Gutzeit —I	Ag salt —II	Iodine —III
Mean $\bar{x}$	-0.20	-0.03	-0.16
Standard Deviation $s_x$	$\pm 0.27$	$\pm 0.20$	$\pm 0.54$
Standard Error $s_x$	$\pm 0.062$	$\pm 0.048$	$\pm 0.121$
Coefficient of Variation $(s_x/\bar{x}) \times 100$	139%	65%	342%
Sample Size $n$	19	17	2
Range	-0.90 to 0.18 (1.08)	-0.37 to 0.42 (0.79)	-2.00 to 0.50 (2.50)

TABLE IV  
Comparison of Analytical Methods  
(Arsenic in vegetation samples)

No.	Gutzeit		Silver Salt		Iodine	
1.	30.8	41.8	35.7	29.8	210.0	194.0
2.	18.6	10.2	14.5	12.3	120.0	142.0
3.	12.0	9.2	4.7	2.5	120.0	112.0
4.	12.0	11.0	3.6	1.7	150.0	120.0
5.	71.0	84.0	114.5	106.0	224.0	142.0
6.	13.8	7.4	2.8	4.5	68.0	74.0
7.	14.6	15.4	8.1	6.3	134.0	174.0
8.	21.0	8.5	4.6	1.7	44.0	52.0
9.	11.8	9.6	1.98	0.75	—	—
10.	9.3	4.0	1.24	0.65	90.0	—
11.	21.3	23.0	16.1	18.6	128.0	120.0
12.	10.6	—	2.8	0.90	44.0	202.0
13.	8.0	6.0	2.8	—	44.0	44.0
14.	12.5	16.8	6.2	3.56	134.0	150.0
15.	6.6	6.8	0.49	0.32	74.0	120.0
16.	18.6	31.0	47.8	—	128.0	90.0
17.	19.1	25.8	28.0	21.2	120.0	112.0
18.	21.3	27.3	21.9	17.8	—	—
19.	8.0	4.0	1.24	0.61	158.0	150.0
20.	11.1	8.8	4.2	3.1	120.0	68.0
21.	40.5	52.0	63.8	57.0	142.0	172.0
22.	6.6	—	1.36	0.39	74.0	104.0
23.	14.6	19.0	8.7	9.2	188.0	164.0
24.	6.6	12.0	3.7	2.7	134.0	120.0
25.	13.3	14.0	5.3	4.8	150.0	150.0
26.	13.3	10.3	6.9	4.6	164.0	172.0
27.	64.0	75.2	78.8	64.0	—	—

The analytical results found are tabulated in Table I.

Considering that these results were obtained by 8 separate analysts in different laboratories, the absolute accuracy may be considered good.

Method No. 3

This is an iodine microtitration with electrical indication of the end point. A millivolt recorder is used together with a transistor amplifier (Dr. B. Lange, West Berlin) and amperometric titrator ("Ampot" E. H. Sargent, Chicago). The

TABLE V

	Vegetation Samples		
Mean	-1.19	2.68	-3.74
Standard Deviation	$\pm 6.59$	$\pm 3.62$	$\pm 44.0$
Standard Error	$\pm 1.32$	$\pm 0.72$	$\pm 9.17$
Coefficient of Variation	555%	135%	1177%
Sample Size	25	25	23
Range	-13.0 to 12.5 (25.5)	-2.50 to 14.80 (17.30)	-158.0 to 72.0 (230.0)

titrant is fed into the sample from a Gilmont microburette. At the endpoint, a sudden pen deflection is observed on the recorder chart. The electrical sensitivity amounts to 0.5 microamperes for full scale deflection.

No sample preparation was required for water samples. Vegetation samples were weighed and digested with oxidizing acid consisting of nitric-sulfuric-perchloric, 48-40-12 by volume. After

digestion, nitric and perchloric acid were removed by bringing the digest to the white fumes of sulfuric, cooling, adding distilled water, and again bringing to white fumes of sulfuric. Digests were made up to 200 ml from which aliquots were taken from comparison of the various methods.

In Table II are shown the results of duplicate analyses on arsenic-containing water samples by the three methods.

The mean difference, standard deviation of differences and coefficient of variation were determined for each method separately, with the results shown in Table III. In Table IV are shown the results of duplicate analyses on separate aliquots of arsenic containing vegetation digests. Similarly, the statistical data for the vegetation samples is shown in Table V.

The water and vegetation analyses indicate Method II as the most reliable of the three, having a lower standard deviation and coefficient of variation. A better statistical picture might

GUTZEIT

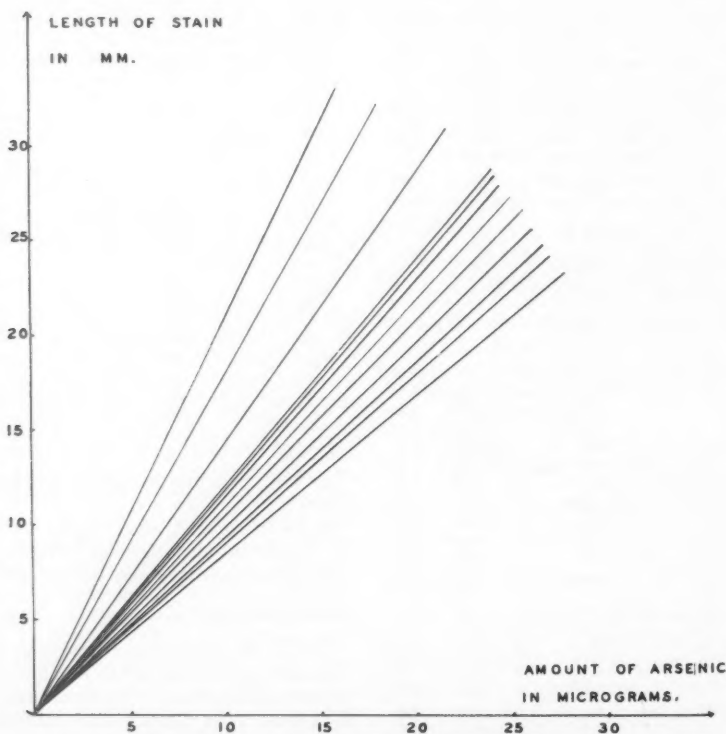


FIGURE 1. Variability of Gutzeit Standard Curves.

have been presented for each of the methods by using a completely artificial experiment on pure arsenic standards. However, it must be remembered that samples actually analyzed are more complex, such as those tabulated in Tables II and IV.

In conclusion the best all round method would appear to be that of Vasak and Sedivec. This method is sensitive, results are more accurate, the standard curve is reproducible from run to run and the method can cover a wide range of concentrations.

The Gutzeit method possesses the advantage of specificity, simplicity of operation, and readily lends itself to large scale analysis. The simplicity of method is deceptive, however, since results are greatly affected by numerous operating variables, such as temperature, rate of gas flow, humidity of gas stream, and catalytic trace elements in the system. These operating variables are not easily controlled in spite of all efforts to do so. It is particularly noticeable that arsenic standards and unknown samples evolve gas at two different rates, the unknowns always being faster. This is probably a catalytic effect as mentioned above. One would then expect the stains for the unknowns to be somewhat longer than the standard for the same amount of arsenic present. There is no simple way of compensating for this misalignment, and in view of the large number of other variables it is probably not worthwhile. A separate standard curve is pre-

pared for each group run under the same conditions. The variability of the standard curve is illustrated by Figure 1.

There is a subjective error inherent in the Gutzeit method. From Table II it may be seen that Gutzeit values for the lowest amounts of arsenic found are generally larger than the values found by Method II. This is due to the fact that at the limit of sensitivity of the Gutzeit method there is a tendency to read the very short stains longer than they actually are.

For suitable samples, such as water, air, and stack effluents, titration is an accurate, reproducible and sensitive method. Substances reacting with iodine, other than arsenic, must be absent. It is noticeable that results by iodine titration are much too high for vegetation digests, but are not too inaccurate for water samples. It comes closer to being an absolute method than the other two, since no standard curve is required and there is essentially no upper limit to the range of arsenic concentrations which may be tested.

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#### Dr. Elda E. Anderson

It is with regret that we announce to our readers that Dr. Elda E. Anderson passed away on April 17, 1961. Dr. Anderson received her M.S. from the University of Wisconsin in 1924 and her Ph.D. in 1941 from the same school. She had been a valued member of AIHA since 1955. In her position as Chief, Education and Training Section, Health Physics Division, Oak Ridge National Laboratories, she was intimately associated with problems of industrial hygiene and radiation protection. Those who knew her through her many fine contributions to these fields join her associates and friends in these expressions of honor and esteem.

# Ultraviolet Spectrophotometric and Fluorescence Data

J. A. HOUGHTON and GEORGE LEE

*Loss Prevention Department, Liberty Mutual Insurance Company,  
Hopkinton, Massachusetts*

Data are presented on the ultraviolet absorption and fluorescence characteristics of a number of substances of interest to industrial hygienists. These properties can be used to make simple and accurate determinations of many materials, although there are limitations because of interferences of other substances. The order of magnitude of the absorptivity will indicate the sensitivity of determination by ultraviolet absorption.

**D**ATA on the ultraviolet absorption and fluorescence characteristics of substances of industrial hygiene interest have been published in various journals, and a summary of data was presented last year in this journal.<sup>1</sup> Where the absorption or emission characteristics are within the range of present day instruments they have proven to be useful for quantitative determinations, particularly for polycyclic aromatic hydrocarbons<sup>2, 3, 4</sup> which absorb ultraviolet strongly.

Although there are limitations, because of interference of other substances with similar characteristics, it is possible to adapt and use these data in the development of industrial hygiene procedures. The additional data presented here was obtained from the literature and from our laboratory and should be useful for other industrial hygiene laboratories.

## Terms and Symbols

The terms and symbols used are those proposed by ASTM Committee E-13.<sup>5</sup>

$$A = abc = \frac{\epsilon}{M} bc$$

$A$  = absorbance (spectrophotometer reading)

$a$  = absorptivity

$b$  = cell light-path length in centimeters

$c$  = concentration in grams per liter

$\epsilon$  = molar absorptivity

$M$  = molecular weight

Presented at the Twenty-second Annual Meeting of the American Industrial Hygiene Association, Detroit, Michigan, April 11, 1961

## Selection of Solvent

The solvent used must have an ultraviolet cut-off point below the peak absorption wavelength of the substance to be determined, but it is not always necessary to use a spectrographic grade of solvent. The workable cut-off point can be determined by placing the solvent in a one-centimeter silica cuvette in a Beckman DU spectrophotometer and determining the lowest wavelength at which the instrument can be balanced. Results from our laboratory on reagent grade solvents from the shelf are shown in Table I with a comparison of figures for spectrograde solvents from Eastman<sup>6</sup> and Matheson.<sup>7</sup> Although spectrograde quality is needed for some

TABLE I  
Ultraviolet Cut-off Values

Solvent	Reagent grade	Spectrographic grade
Acetone.....	327 m $\mu$	330 m $\mu$
Benzene.....	279	280
$\eta$ -Butanol.....	268	210
Carbon tetrachloride.....	263	265
Chloroform.....	245	245 (250)
Ethanol, USP.....	219	—
Ethanol, 3A.....	219	—
Isooctane.....	220	210 (220)
Isopropanol.....	218	210
Methanol.....	218	210
Methyl ethyl ketone.....	327	—
Nitric acid—6N.....	334	—
Sulfuric acid—6N.....	215	—
Trichloroethylene.....	287	—
Tetrachloroethylene.....	292	290 (295)
Toluene.....	285	285
Water.....	212	—

TABLE II  
Ultraviolet Absorption

Substance	MAC micrograms per liter of air	Max ma wave- length milli- microns	Log $\epsilon$	$\epsilon$	$\alpha$	$c \times 1000$ micro- gram per milliliter of solu- tion	Solvent	Ref
Acetaldehyde	360	290	1.20	15.9	0.36	140	Hexane	13
Acetone	2400	265	1.24	17.6	0.30	165	Water—acidic	12, 14
		272	1.17	14.8	0.26	195	Ethanol (3A)	12
		272	1.19	15.5	0.27	190	Ethanol	14
		278	1.11	12.9	0.22	230	Cyclohexane	14
		279	1.17	14.8	0.26	190	Hexane	14
		280	1.14	13.8	0.24	210	Hexane	13
Acetophenone	(98)	245.5	3.09	9800	82	0.74	Water	13
Acetyl chloride	(3.2)	240	1.53	34	0.43	116	Hexane	13
Acrolein	1.2	<208	—	—	—	—	Hexane	13
		328	4.10	12600	225	0.22	Ethanol	13
Arochlor 1254	—	<213	—	—	164	0.3	Isooctane	12
Benzaldehyde	—	240	4.15	14100	133	0.38	Ethanol	13
		283	3.25	1780	17	3	Ethanol	13
		250	4.06	11400	108	0.46	Water	13
Bromobenzene	—	210	3.90	7900	50	1	Water	13
		261	2.28	192	1.2	42	Water	13
		265	2.39	243	1.6	35	Hexane	13
1,3-Butadiene	2200	217	4.32	21000	390	0.13	Hexane	13
o-Chloroaniline	—	290	3.43	2700	21	2.3	Hexane	13
o-Chloroaniline (sulfate)	—	232	3.86	7240	57	0.9	Water—pH 8	12
		286	3.34	2320	18	2.8	Water—pH 8	12
m-Chloroaniline	—	291	3.32	2090	16.5	3	Hexane	13
m-Chloroaniline (sulfate)	—	236	3.90	7920	62.2	0.8	Water—pH 8	12
		286	3.30	1990	15.6	3.2	Water—pH 8	12
p-Chloroaniline	—	239	4.07	11700	92	0.54	Water	13
		290	3.18	1500	12	4.2	Water	13
		297	3.31	2040	16	3	Hexane	13
p-Chloroaniline (sulfate)	—	240	4.06	11400	89.2	0.6	Water—pH 8	12
		291	3.21	1620	12.7	4	Water—pH 8	12
Chlorobenzene	350	265	2.49	310	2.8	18	Hexane	13
o-Chlorotoluene	(388)	266	2.59	390	3.1	17	Hexane	13
m-Chlorotoluene	(388)	267	2.58	380	3	17	Hexane	13
		267	2.43	272	2.1	23	Ethanol	12
		275	2.35	223	1.8	30	Ethanol	12
p-Chlorotoluene	(388)	271	2.84	690	5.5	9	Hexane	13
		270	2.65	450	3.6	14	Ethanol	12
Cyclohexanone	400	289	1.20	16	0.16	310	Hexane	13
		282	1.23	17	0.17	290	Methanol	13
o-Dichlorobenzene	300	271	2.57	372	2.5	20	Hexane	13
		<218	—	—	—	—	Isopropanol	12
		270	2.49	308	2.1	24	Isopropanol	12



TABLE II—Continued

Substance	MAC micrograms per liter of air	Maxima wave- length milli- microns	Log $\epsilon$	$\epsilon$	$a$	$c \times 1000$ micro- gram per milliliter of solu- tion	Solvent	Ref
<i>m</i> -Dichlorobenzene	—	271	2.98	954	6.5	8	Hexane	13
		271	2.59	392	2.7	19	Isopropanol	12
		264	2.44	—	—	—	Isopropanol	12
		280	2.37	—	—	—	Isopropanol	12
<i>p</i> -Dichlorobenzene	450	273	2.60	399	2.7	18.5	Hexane	13
		224	4.11	12900	87.6	0.57	Isopropanol	12
		266	2.48	304	2.1	24	Isopropanol	12
		273	2.62	417	2.8	18	Isopropanol	12
Diethyl ketone	—	270	1.34	22	0.26	195	Water	13
		275	1.28	19	0.22	230	Methanol	13
		280	1.25	18	0.21	240	Hexane	13
<i>m</i> -Dinitrobenzene	1	242	4.21	16300	97.0	0.52	Water	13
		305	3.04	1100	6.5	7.7	Water	13
<i>p</i> -Dinitrobenzene	1	266	4.16	14500	86.3	0.58	Water	13
Diphenyl	—	246	4.31	20300	130	0.4	Hexane	13
		252	4.26	18300	120	0.4	Chloroform	13
Diphenyl oxide	—	280	3.28	1905	11.2	4.5	Cyclohexane	13
Furan	—	200	4.00	10000	147	0.34	Hexane	13
		250	0.0	1	0.015	3400	Hexane	13
Furfuryl alcohol	(200)	217	3.88	7640	78	0.64	Water	12
Hydroquinone	2	295	—	—	—	—	Hexane	13
		294	3.55	3560	32.4	1.5	Isopropanol	12
Iodoform	—	274	3.09	1230	3.1	16	Chloroform	11
		307	3.21	1610	4.1	12	Chloroform	11
		347	3.26	1820	4.6	11	Chloroform	11
Isophorone	140	244	4.09	12300	90	0.6	Water	12
		235	4.11	13000	94.5	0.53	Isopropanol	12
Isoprene	(2200)	220	4.38	24000	350	0.14	Hexane	13
Mesityl oxide	100	314	4.76	58000	593	.09	Ethanol	13
		230	4.10	12600	129	0.4	Hexane	13
<i>N</i> -Methyl aniline (sulfate)	9	238	3.98	9510	88.9	0.6	Water—pH 8	12
		286	3.22	1650	15.5	3.2	Water—pH 8	12
Methyl ethyl ketone	740	272	1.30	20	0.27	185	Ethanol	12
		275	1.34	21.8	0.30	167	Isopropanol	12
		268	1.28	19	0.26	190	Water	12
		267	1.31	20.4	0.28	175	Water	13
		272	1.25	17.8	0.25	200	Methanol	13
Methyl hexyl ketone	—	276	1.34	21.9	0.17	290	Methanol	13
		270	1.41	25.7	0.20	250	Water	13
Methyl iodide	(58)	260	2.60	400	2.8	18	Hexane	13
Methyl isobutyl ketone	410	246	1.77	58.4	0.58	86	Water	12
		237	1.74	54.9	0.55	90	Isopropanol	12
		279	1.40	25.1	0.25	200	Isopropanol	12
Methyl propyl ketone	—	277	1.33	21.4	0.25	200	Ethanol	13
		270	1.33	21.4	0.25	200	Water	13

TABLE II—Continued

Substance	MAC micrograms per liter of air	Maxima wave- length milli- microns	Log $\epsilon$	$\epsilon$	$a$	$\epsilon \times 1000$ micro- gram per milliliter of solu- tion	Solvent	Ref
alpha-Methyl styrene	480	245	4.0	10000	85	0.6	—	13
beta-Methyl styrene	480	245	4.0	10000	85	0.6	—	13
o-Methyl styrene	480	245	4.10	13000	110	0.5	—	13
Nitrate ion	(25)	302	0.84	7	0.11	455	Water—basic	15
Nitrite ion	—	211	3.76	5800	126	0.4	Water—pH 7	15
		211	3.30	2000	44	1	Water—pH 2	15
		355	1.36	23	0.5	100	Water—pH 6 to 12	15
o-Nitroaniline	(6)	245	3.85	7000	50.6	1	Water	13
		283	3.73	5400	39.1	1.3	Water	13
		412	3.65	4500	32.6	1.5	Water	13
m-Nitroaniline	(6)	246	4.03	10700	77.5	0.65	Water	13
		280	3.68	4800	34.8	1.4	Water	13
		358	3.16	1450	10.5	4.8	Water	13
p-Nitroaniline	(6)	226	3.83	6700	48.6	1	Water	13
		381	4.13	13500	98	0.5	Water	13
Nitrobenzene	5	269	3.89	7800	63.5	0.8	Water	13
		262	3.86	7300	59.3	0.9	Methanol	12
Nitromethane	250	270	1.15	14	0.23	220	Dilute HCl	13
o-Nitrotoluene	30	221	3.64	4400	32	1.6	Water	13
		266	3.72	5300	39	1.3	Water	13
		325	3.11	1300	9.5	5.3	Water	13
m-Nitrotoluene	30	221	3.76	5700	41.6	1.2	Water	13
		273	3.86	7300	53.3	0.9	Water	13
		315	3.11	1300	9.5	5.3	Water	13
p-Nitrotoluene	30	217	3.83	6700	49	1	Water	13
		285	3.97	9250	68	0.7	Water	13
o-Phenylene diamine	(0.44)	205	4.60	40000	370	0.13	Water	13
		233	3.84	6900	64	0.8	Water	13
		289	3.46	2900	27	1.8	Water	13
m-Phenylene diamine	(0.44)	210	4.57	37000	340	0.15	Water	13
		240	3.86	7300	68	0.74	Water	13
		289	3.32	2100	19.5	2.5	Water	13
p-Toluidine	(22)	232	3.95	8900	83	0.6	Water	13
		286	3.20	1600	14.9	3.4	Water	13
		293	3.29	1950	18.2	2.7	Hexane	13
Tricresyl phosphate	—	<212	—	—	>94	0.5	Isooctane	12

materials, the standard reagent grades are satisfactory for most materials.

Reagent grade solvents can frequently be purified in the laboratory for special use.<sup>10</sup> Practical grade isooctane (1,1,1 trimethyl pentane) can be purified by passing it through a column of silica gel,<sup>8</sup> and the ultraviolet cut-off point lowered from 220 to 210 millimicrons.

Solvents other than those listed in Table II may be more readily adapted to air sampling procedures, but the peak wavelengths and absorptivity in other solvents will differ from the data given. The data presented indicate the order of magnitude of the absorbaney, even though another solvent may be used, and give

indications of the ease and sensitivity of measurement.

For example, values are given for methyl ethyl ketone in ethanol, isopropanol and water and these solvents can be used for air sampling; but a similar magnitude of absorbancy would be obtained if an industrial hygienist decided that a higher alcohol or another solvent was better suited to his conditions. Data on nitrobenzenes in water are presented, but this solvent would not be satisfactory for air sampling of these materials. The use of another solvent such as isooctane should show similar strong absorptivity and this solvent or a similar one should be suited to air sampling because of the greater solubility.

#### Air Sampling

Some of the data cannot be adapted directly to air sampling procedure, and additional information is needed before a satisfactory procedure can be set up. A stronger absorptivity may be desired, and it may be possible to increase the absorptivity by proper selection of solvent or by adjustment of pH, but ideas that are promising do not always work out. Nitromethane in dilute hydrochloric acid has a low absorptivity; in basic solution the absorptivity is increased but unfortunately this compound and similar aliphatic nitro compounds are not stable in alkali.<sup>9</sup> Other compounds in solution, such as furfuryl alcohol in water, may slowly decompose and affect the results if there is an appreciable time lapse between sampling and analysis. These possibilities must be investigated because most of the data in the literature was determined on freshly prepared solutions.

Silica gel is more convenient to use in the field than a solvent in a gas washing bottle or bubbler particularly where the sample has to be carried or shipped for some distance. It may take a few trials to determine the proper solvent for the removal of the sample from the silica gel, but there should be very few instances where this would be a serious problem.

TABLE III  
Fluorescence

Substance	Activation wavelength microns	Emission wavelength microns	$c \times 1000$ micrograms per milliliter of solution	Solvent	Ref.
o-Chloroaniline.....	225	525	3	Water—pH 8	12
m-Chloroaniline.....	255	525	3	Water—pH 8	12
Hydroquinone.....	285	330	.03	Water	12
N-Methyl aniline....	285	350	0.2	Water—pH 8	12

Ketones, for example, can be removed from silica gel by the use of isopropanol as indicated by Elkins.<sup>10</sup> Isophorone will be removed slowly from silica gel, but by letting it stand for 48 hours practically 100% can be recovered for analysis; other ketones may be removed from silica gel in shorter time.

The ultraviolet method is best suited for substances with a strong absorptivity, but it can be used for the determination of substances with a relatively weak absorption such as acetone or methyl ethyl ketone where high sensitivity is not needed. Acetone in water has an absorptivity of about 0.3, and 165 micrograms of acetone per milliliter of water can be determined if 25 liters of air, containing a concentration of 100 ppm (240 micrograms per liter), were sampled and collected in 25 milliliters of water, this concentration would be more than adequate for analysis. With a threshold limit of 1000 ppm, it would seldom be necessary to make an accurate determination less than 100 ppm, and the ultraviolet method and the accuracy would be good above 100 ppm.

Ultraviolet and fluorescence procedures can be used at times to shorten chemical procedures. Instead of titration, the ultraviolet absorption of iodoform can be used as a measurement in the determination of acetaldehyde and acetone. Ultraviolet methods have been adapted as standard by the ASTM for several materials<sup>17, 18, 19, 20</sup> and similar procedures can be set up for industrial hygiene.

#### Data in Tables

The values for " $c \times 1000$ " in Table II are for an absorbance reading of 0.05 on the Beckman DU spectrophotometer.

The fluorescence data was obtained on an Aminco-Bowman spectrophotofluorimeter and the concentrations shown in Table III were obtained with relative readings of 0.05 on this instrument.

The curves for concentrations vs. absorbance readings will be straight lines for substances given in Table II except where the solution fluoresces. Chloroaniline and hydroquinone in solution fluoresce and the emitted fluorescent light will affect the phototube of the spectrophotometer and the calibration curves will not be a straight line.

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## AIR POLLUTION TRAINING

THE PUBLIC HEALTH SERVICE, through its Division of Air Pollution, will conduct a 2-week training course in "Control of Particulate and Gaseous Pollutants," October 23-November 3, 1961, at Cincinnati, Ohio, for officials, engineers, and professional personnel interested in the control problem. Instruction covers the fundamental mechanisms for removal of potential atmospheric pollutants from a gaseous effluent by means of large scale equipment, methods of predicting the overall efficiencies of collectors, and ways of estimating the composition of the final emission. Covered also are performance and applicability of inertia-type and other equipment, with emphasis on information which enables a trainee to predict and analyze the performance of existing control equipment and to select that appropriate for new installations.

Full description of the course is given in the *Training Program Bulletin* which is available on request. Address applications for the course or requests for information to the Chief, Training Program, Robert A. Taft Sanitary Engineering Center, 4676 Columbia Parkway, Cincinnati 26, Ohio, or to a PHS Regional Office.

# Combination Hot Plate and Hood for Multiple Beaker Evaporations

W. B. HARRIS, E. E. CHRISTOFANO, and M. LIPPMANN

*Health and Safety Laboratory, U. S. Atomic Energy Commission, New York, N.Y.*

A combination hot plate and hood for beakers is described which effectively captures gases and vapors evolved during wet digestion and evaporation operations. Four-foot long modules accommodating 250, 400, and 600 ml Griffin form beakers were constructed and installed in the space below the reagent shelf between laboratory benches placed back-to-back. The location minimizes air turbulence, permitting complete control with as little as 15 cfm of air per linear foot of hood. The beakers rest directly on resistance strip heaters with controlled heat output.

## Introduction

THE Analytical Division of the Health and Safety Laboratory performs numerous routine chemical and radiochemical analyses on air, biological, and environmental samples containing toxic and radioactive constituents. It is not uncommon, for example, to have several hundred such samples in process at the same time. Most of the procedures call for digestion and evaporation steps which take place in Pyrex beakers. Usually, the first step is the destruction of all unwanted organic matter such as filter paper in an air sample, or normal biological residues. To eliminate the organic matter with minimum volatilization of the material being analyzed, the samples are wet-ashed. This technique may involve the use of nitric, sulfuric, perchloric acids or combinations of these at elevated temperatures. Thus, provision must be made for the capture and removal of the highly corrosive acid fumes and water vapor evolved during heating and evaporation and also any toxic and/or odorous materials which may be evolved.

The large numbers of such digestions and evaporations carried out by the analytical group in routine analysis makes the use of conventional open-faced laboratory hoods impractical. It is difficult to introduce, observe and remove large numbers of small beakers from such hoods safely and efficiently, and furthermore, a very large volume of exhaust air is required for effective control. The first solution of the problem which was evolved is the combination hot plate and local exhaust hood illustrated in Figure 1. It was designed to accommodate Griffin form beakers of 125, 250, and 400 milliliters capacity or any other laboratory-type glassware whose lip height approximates these beakers.

With this device it was possible to carry out 60 small beaker evaporations within the space formerly occupied by a 4-foot wide hood, and still have each beaker readily accessible for observation, introduction or withdrawal.

After the four-step hood was successfully used for about two years, it became necessary to move the laboratory to new quarters. This required a reevaluation of the original design to make it more suitable to the entire laboratory operation. It was decided that it would be useful to have such a device available to each chemist, but available in such a way as not to use any bench space. A small prototype unit (Figure 2) was constructed to demonstrate the principle and to provide an experimental model for determining optimum air flow.

## Design Objectives

The design objectives may be briefly stated as follows:

- (1) A temperature regulated heating surface to permit controlled evaporation.
- (2) Effective capture of evolving gases and vapors.
- (3) Unobstructed observation of the proceeding evaporation.
- (4) Optimum space utilization.
- (5) Convenience of location to permit efficient loading and unloading, yet out of the way of other operations.
- (6) Provision for servicing, including changing of hot plate heaters and decontamination after accidental spillage.

## Physical Description

Utilizing the experience gained from the experiments with the prototype, the basic hood





FIGURE 1. Four-step hot plate and hood combination.

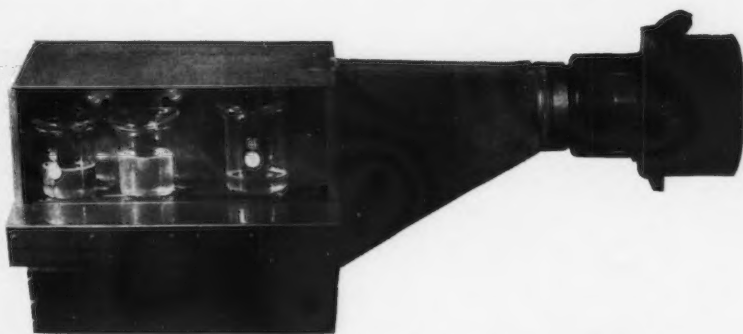


FIGURE 2. Prototype model of between-the-bench type hood.

was designed as a 4-foot long modular unit for 250, 400, and 600 milliliter beakers. Sixteen such modules were constructed of 1/32" thick, Type 316 stainless steel sheet. They occupy space under the reagent shelves between laboratory benches placed back to back, and present a working surface to each bench. An eight-foot laboratory bench with two modular units is shown in Figure 3. Figure 4 shows the hoods during installation with the nearer laboratory bench removed. Note the wiring and duct connections. Figure 5 shows the floor plan of the standard laboratory of the Analytical Division.

Each bay is occupied by one chemist and is provided with eight linear feet of beaker hood space. The position of the hood at the rear of the bench permits ready access to the beakers without interfering with other operations on the bench. The location also minimizes air currents at the beaker caused by movement in the bay. All the beakers are directly visible to the chemist working in the bay. Ventilation air is drawn past the beaker lips, enters the plenum of the hood through a series of holes, and passes through a transition section into the exhaust duct running near the floor. The major dimensions of the



FIGURE 3. Standard Health and Safety Laboratory four-foot modular units.



FIGURE 4. Modular units during installation.

## TYPICAL ANALYTICAL LABORATORY

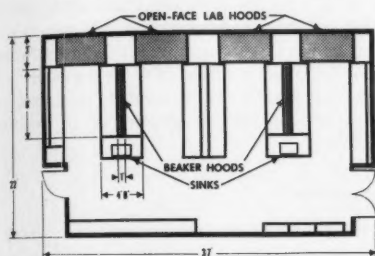


FIGURE 5. Floor plan of typical laboratory.

standard Health and Safety Laboratory hood are shown in Figure 6.

While the four-foot modular units described provide the Health and Safety Laboratory with the desired flexibility in arranging laboratory space, this type of hood could be made in any other size desired. The geometry of the glassware to be handled would determine the depth of heating surface and the clearance height required. The most practical lengths are multiples of strip heater lengths. Standard strip heaters are available in lengths ranging from eight inches to forty-three inches and are 1½ inches wide. The standard Health and Safety Laboratory four-foot module uses four 23½ inch strip heaters

on each side, giving a heating area of approximately 280 square inches per module.

*Airflow*

Airflow measurements performed on the prototype unit indicated that, at 15 cubic feet per minute per linear foot of hood, all of the material evolved from a 600 milliliter beaker placed at maximum heat would be captured. To provide a safety factor, the hoods were designed for 20 cubic feet per minute per linear foot. Each foot of length can accommodate three 600 milliliter or four 250 milliliter beakers.

*Plumbing*

The Transite exhaust duct was installed with a slight pitch and a drain line was attached to the low end to facilitate removal of condensed vapors.

*Heating Elements*

The heating surface of each side of each hood is composed of four standard iron-sheath strip resistance heating elements which are supported by blocks of Transite. Strip heaters have the advantage over standard laboratory hot plates in reduced size and cost, and in ease of replacement. Each strip heater is rated at 300 watts. With the switch in the "high heat" position and

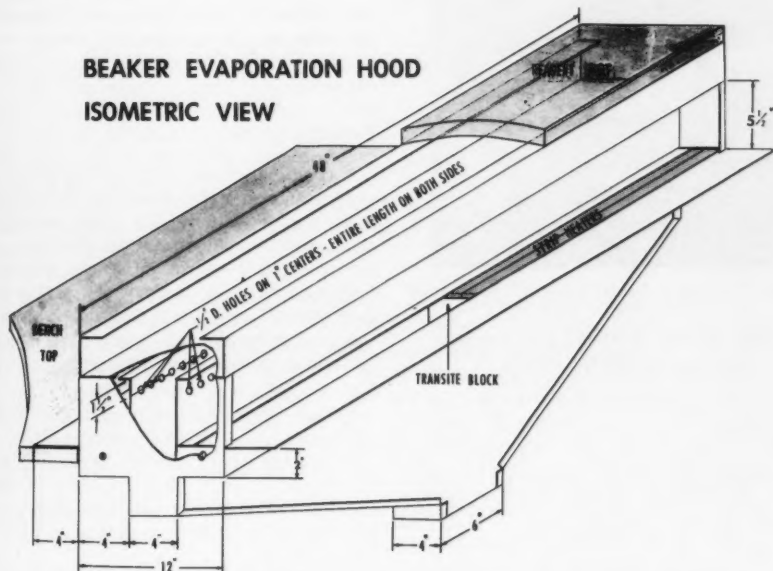
BEAKER EVAPORATION HOOD  
ISOMETRIC VIEW

FIGURE 6. Isometric drawing of standard module.

the beakers resting on two adjacent heaters, rapid evaporation takes place without vigorous boiling. If higher heat levels were desired, 500 watt strips could be substituted for the 300 watt units.

#### Electrical Connections

The heating elements on each side of each 4-foot module are controlled by separate circuit breakers and switches with four positions; off, low, medium, and high. In the "high" position, all four heaters are connected in parallel; in "medium" pairs of heaters in series are connected in parallel; and in "low" all four heaters are connected in series. These heat controls have proved satisfactory, although it should be noted in retrospect that control could have been effected with greater simplicity and lower cost by using variable transformers, giving a continuous temperature range between ambient and maximum temperature. All current carrying wire within the hood is #12 AWG Silicone rubber 200°C appliance wire with glass fibre braid connected through 3/4 inch Sealite cables.

#### Cost

Each four-foot module costs \$155 uninstalled. This price was based on sixteen units and would

vary with quantity. The strip heaters cost \$3 each or \$24 per module. The heat-control switching system cost approximately \$75 per module, while control through variable transformers would have been about \$30 per module. The ventilation duct work, air mover, plumbing, and wiring costs are greatly dependent on local conditions.

#### Performance

Sixteen four foot modular units have been in use in the Health and Safety Laboratory for approximately 1½ years. During this time they have performed satisfactorily in all respects. With 15 to 20 cubic feet per minute of exhaust air per linear foot of hood space, complete control of evolving gases and vapors has been achieved. This corresponds to 120 to 160 cubic feet per minute of air per four-foot modular section. Spillage from cracked glassware is confined in a tray beneath the strip heaters and is readily removable. All of the original strip heaters are still in service. Heat levels obtained in the three positions have been adequate for all applications.

#### Related Applications

Figure 7 shows an exhaust hood for separatory funnels designed by Ayerst, McKenna and Harrison, Biological and Pharmaceutical Chemists of Montreal, Canada. This hood was designed on the basis of photographs and descriptive material supplied by the Health and Safety Laboratory.

#### Summary

A combination hot plate and hood for multiple evaporations has been described. It permits large scale beaker evaporations with minimal ventilation requirement, maximum efficiency and accessibility, and utilizes otherwise wasted space between laboratory benches. Two other types of local exhaust hoods were illustrated which utilize the same principle. It is believed that many similar applications can be developed.



FIGURE 7. Local exhaust hood for separatory funnels.

(Courtesy Ayerst, McKenna and Harrison, Limited, Montreal, Canada)

# A Comparison of Particle Size Measurements

E. J. BAIER, B.S., M.P.H.

*Division of Occupational Health, Pennsylvania Department of Health,  
Harrisburg, Pennsylvania*

The determination of particle size is essential to the evaluation of airborne dust hazards. A set of 18 slides was prepared and circulated among 30 persons of varying experience in particle size determination. They made 206 particle size determinations. Statistical evaluation of the results are presented. Industrial hygienists with very little or very much experience in the total field of industrial hygiene demonstrated the greatest variance of measurement. Those in the experienced group are primarily in the supervisory category, and their errors appear to be due to a lack of constant use of the microscope. Practice, rather than experience, seems to be the main criterion of accuracy in particle size measurement.

## Introduction

IT IS necessary to measure the particle size of airborne dust in order to determine adequately the hazard involved. This paper describes one method of comparing measurement techniques and results. The use of this method provides certain data concerning reliability of particle size measurement.

In order to assess the degree of hazard of airborne silicosis-producing dusts three factors are of importance—the free silica or, in some cases, the silicate content; the concentration; and the particle size. The silica content may be determined by petrographic technique, x-ray diffraction, or by chemical means. Airborne exposure standards, or maximum allowable concentrations, are based on the silica content. The concentration may be found by a variety of techniques, the most common of which in the United States is the dust count by means of the light-field, microscopic method.<sup>1</sup>

When both the silica content and concentration are known, the degree of hazard may then be evaluated. This may be adequate when the concentration is far less than the maximum allowable concentration, but this limit is frequently exceeded. In these instances evaluation of the degree of hazard is erroneous unless the size distribution of the particulate cloud is determined.

The respiratory system is selective regarding deposition of particulates. The smaller particles

tend to behave as a fluid and move into and out of the lungs with the air. The large particles are removed in the nose and upper respiratory system. We are therefore concerned with those particles which are small enough to enter the alveoli and also large enough to be deposited there. To evaluate the hazard, we must know the particle size distribution.

Many methods have been advocated for particle size measurement, including electron microscopy, microprojection, and photo and optical microscopy. Various combinations of ocular and objective lens are prescribed for optical systems, and various eyepiece graticules and ocular micrometers are available.<sup>2</sup> In addition, various oils, which have different indices of refraction from the substance to be sized, may be used. Most industrial hygienists use optical methods for determining a particle size distribution of a dust cloud.

Since the particles in a dust cloud are not uniform in size, the median size is an aid to the assessment of the degree of hazard. It defines whether or not the median particle can enter an alveolus and be deposited.

The median in itself is not adequate however. The range of size is an important consideration. Drinker and Hatch<sup>1</sup> suggest a logarithmic plot of diameter measurements on probability graph paper as a means of defining the median particle size and the distribution range. Using this technique the 50 per cent size is both the median and the geometric mean by definition. The standard geometric deviation, or range, is then defined from the plot as the 84.13 per cent size divided by the 50 per cent size. This results in a

Presented at the Twenty-second Annual Meeting of the American Industrial Hygiene Association, Detroit, Michigan, April 1961.



more rapid technique than is possible by calculation.

In order to compare various techniques of measurement and their results, a set of slides was prepared and circulated. Thirty persons participated in this project; twenty-one conducted 5 or more measurements and five evaluated 10 or more. In several instances the same slide was analyzed by the same individual, without his knowledge, several times. This project was conducted over a fourteen month period, and 206 particle size determinations were made. Each determination involved the linear measurement of more than 200 particles.

### Procedure and Methods

Air samples which had been collected by means of membrane filters and Greenburg-Smith impingers were used exclusively for this project. A section of the membrane was placed on a standard 3 inch by 1 inch microscope slide. A drop of plastic cement was used to clear the membrane, and a cover slip was placed over the membrane. A permanent mount was then available for study. In the case of impinger samples, approximately 3 cc of ethyl alcohol was placed on a standard microscope slide and evaporated under an infrared heat lamp. One cc of xylol was then placed on the slide to clear it, and the solvent was evaporated. A cover slip was affixed by plastic cement along the edges to make a permanent mount.

Eighteen slides were used in the project. Most of the slides were available from previous industrial hygiene surveys of foundries, brick-yards, and coal mines, although five were specially prepared in the laboratory.

Initially, each slide was wrapped in a soft absorbent paper towel and mailed to the examiner. A form, Figure 1, was prepared and sent with the sample slide. The form was to explain the purpose of the project and to obtain information concerning the technique used. In the initial mailing three slides were damaged prior to analysis and three slides were damaged during return. To counteract this, wooden laths slightly larger than the slides, were made and placed, sandwich style, over the slide to protect it. The sandwich was held together by rubber bands. When this was placed in the paper packaging, no further breakage occurred during transit.

The method of particle size measurement was left exclusively to the examiner. A 10× ocular and 95× (N.A. = 1.25) objective lens, with oil, was the most commonly used system. This was followed closely by a system using a 30× compensation ocular and 95× objective lens, with

oil. Some examiners sized particulate sample slides by means of a 15× ocular and 95× objective lens, (with oil), a 10× ocular and 44× (N.A. = 0.85) objective lens (high dry technique), and a microprojector, but these were in the minority of preference. All microscopes were equipped with Abby condensers. A filar micrometer or Porton eyepiece graticule was used for all linear size measurement.

### Results

#### Group Study

Table I shows the composite findings for each of the 18 slides. Each of the median particle size values for each slide reported was averaged and a median value was determined. In general, the average and median values were found to be similar, indicating that the median particle size determined for each slide probably followed a normal distribution. The same was found to be true for the calculated standard deviation for each slide.

Assuming normal distribution, approximately two-thirds of all of the observations should fall within one standard deviation of the mean, 95 per cent should fall within two standard deviations, and 99 per cent should fall within three standard deviations. In order to determine the validity of a single particle size measurement, the standard deviation of the mean for each slide was calculated using the general formula:<sup>2</sup>

$$\text{Standard deviation}^2 = \frac{\sum(x - \bar{x})^2}{(n - 1)}$$

where  $x$  represented each observation,  $\bar{x}$  represented the mean for each slide, and  $n$  represented the number of observations.

The three standard deviation ranges were then computed for each slide. An analysis of these data is presented in Table II. The number of determinations falling below or above the range was much greater than anticipated. In some cases this was due to loss of definition of the particle by use of microprojector technique. Most of these examinations resulted in a median particle size in excess of the range for the following reasons: the smaller particles were blurred to the extent that they were not capable of being seen and evaluated, the small particles tended to flocculate and appeared as one large particle, or the size of the particles appeared to be larger than was in fact the case. Most of the observations beyond the calculated range were due to individual technique.

Of the 30 persons who participated in this

### Particle Size Comparison Study

On several occasions the question of particle size of airborne particulates was discussed. Recently, it was decided that slides be circulated to Industrial Hygienists so that a comparison can be made.

It is the attempt of this project to determine variance between different sizing techniques. Will you please supply the data requested below concerning the enclosed slide and return this sheet and the slide to me at your earliest convenience. You are to do this without consultation so that it will be valid.

Slide No. \_\_\_\_\_ By \_\_\_\_\_ Date \_\_\_\_\_

How Done: Porton\_\_\_\_\_ Filar Micrometer\_\_\_\_\_ Other: Specify\_\_\_\_\_

Ocular \_\_\_\_\_ × Objective \_\_\_\_\_ × Oil \_\_\_\_\_ Dry \_\_\_\_\_

[illegible]

### Median particle size

Standard deviation

FIGURE 1. Particle size comparison study.

project 9 were within the calculated range at all times, and 20 were within the range in all observations with the exception of two or less. The exceptions were those persons with very little or very much experience in the total field of industrial hygiene.

Of the number of slides sized by four relatively inexperienced persons who were trainees, 12 of 29 measurements were beyond the range; of those sized by five experienced industrial hy-

gienists, 16 of 41 were beyond the range. The errors of the inexperienced are readily understandable. They are in the process of learning the technique and adapting the principles. The errors of the experienced appear to be due to a lack of constant use of the microscope. This latter group is primarily in a supervisory category. They are responsible for carrying out the entire program, and they therefore delegate the task of particle size measurement to a subordi-

TABLE I  
Summary of Particle Size Measurements

Slide Number	Frequency of Measurement	Median Particle Size (Microns)			Standard Deviation		
		Average	Median	Range	Average	Median	Range
1	18	0.70	0.69	0.42-1.25	2.21	2.18	1.6-2.72
2	5	0.69	0.55	0.42-1.35	1.75	1.67	1.32-2.2
3	2	0.96			3.77		
4	18	0.71	0.60	0.40-1.63	2.43	2.29	1.96-3.37
5	8	0.90	0.93	0.48-1.58	2.9	2.97	1.99-4.35
6	none						
7	none						
8	1						
9	19	0.94	0.87	0.42-2.41	2.66	2.48	1.67-4.8
10	1						
11	28	0.74	0.71	0.39-1.40	2.32	2.34	1.49-3.42
12	22	0.81	0.89	0.39-1.31	2.82	2.77	1.3-4.84
13	21	0.80	0.70	0.52-1.78	2.33	2.42	1.61-2.90
14	12	0.65	0.60	0.42-1.24	2.35	2.33	1.54-2.98
15	21	0.81	0.70	0.44-1.32	2.01	1.86	1.52-3.93
16	20	0.76	0.70	0.38-1.44	2.43	2.44	1.59-4.72
17	none						
18	9	0.89	0.57	0.47-1.8	3.27	3.41	2.09-4.10

TABLE II  
Statistical Analysis of Particle Size Measurement

Slide Number	Approximate 99% Range	Number of slides:		
		Within Range	Below Range	Above Range
1	0.5-0.9	11	4	3
4	0.4-1.1	17	0	2
5	0.5-1.3	6	1	1
9	0.2-1.6	18	0	1
11	0.5-1.0	19	5	4
12	0.6-1.0	14	4	4
13	0.5-1.2	17	0	4
14	0.5-0.8	8	2	2
15	0.4-1.2	19	0	2
16	0.4-1.1	16	1	3
18	0.1-1.7	7	1	1

nate. Particle size determination must be accomplished at frequent intervals, not just on occasion. Industrial hygiene experience in itself does not appear to be a primary criterion, but rather practice in measuring particle size.

There were few differences as to type of technique employed in measuring whether or not a specific particle size fell within the calculated range. Considering the frequency of usage, the percentage of measurements falling within the calculated range was independent of the magnification, that is, the combination of ocular and objective lenses used, and for the most part, independent as to whether an eyepiece graticule

or an eyepiece micrometer was used. A higher percentage of particle size determinations made by means of a graticule was within the range than was the case when made by means of a micrometer. This was probably due to fatigue, since the micrometer requires more frequent eye movement from the particle under observation to the micrometer scale and back than does the graticule technique; but the percentage difference found was of the order of 10 per cent.

#### Individual Study

To compare the ability of the examiner to reproduce a particle size measurement, a slide was frequently returned to the same examiner without his knowledge of having already made a determination. This was done in a random procedure. Twenty-one of the thirty participants sized the same slide at least twice, five the same slide 3 times, and one the same slide 4 times. Six sized two slides twice, one sized three slides twice, and one sized four slides twice. In addition, three examiners sized one slide 3 times and one slide twice.

Of the 93 determinations made, 74 were within the calculated range described above. The examiners' findings were either in the range at all times or out of the range at all times with the exception of 4 instances. In general, these differences were not significant, the greatest being 0.6 micron between two particle size measurements made on the same slide by the same individual. Those within the range exhibited even less difference, of the order of 0.4 micron. For example, the results of one slide sized by one examiner were reported as having a median particle size of 0.54, 0.54, 0.70, and 0.83 micron respectively. Although reproducibility appeared to be good, plus or minus 50 per cent of the average of determinations for a single slide, when the same technique was used, the greater differences appeared when different techniques were employed.

The greatest differences were found when a given slide was evaluated by a graticule the first time and a micrometer the second, or when oil immersion was used for one determination and high-dry technique was employed during the second evaluation. Although the differences appear significant by percentage calculation, the differences are of the same order of magnitude.

#### Resolving Power of the Microscope.

The ability of an observer to size dust particles is frequently questioned. What is the smallest particle that an observer is capable of discerning?

In theory<sup>4</sup>, the microscope is capable of magnifying a dust particle to infinity. If, however, the particle becomes indistinct, further magnification only serves to increase the loss of detail. The limitation, therefore, is resolving power, and not magnification. Resolving power depends on the design of the objective lens, or its numerical aperture (N.A.), and the wavelength of the light source. The resolving power, or limit of resolution as it is sometimes called, varies directly with the wavelength (increasing as the wavelength of light approaches ultraviolet) and varies inversely with the numerical aperture, according to the following formula:

Resolving power

$$= \frac{0.61 \times \text{wavelength of illumination}}{\text{numerical aperture}}$$

In this project, the light source most frequently used was a lamp manufactured by American Optical Company equipped with a blue filter. The wavelength of the filter was 0.41 micron as determined by means of a ratio recording spectrophotometer. By use of the formula, the limit of resolution for the 95× objective lens (N.A. = 1.25) was to be approximately 0.2 micron and the limit of resolution for the 44× objective (N.A. = 0.85) was found to be approximately 0.3 micron. In practice, however, these calculated values were not found to be true. There is one other very important factor which is not taken into consideration. That is the observer himself.

Recently an associate (Mr. Robert Diakun, Industrial Hygienist III, Pennsylvania Department of Health), in reducing particulate size data using logarithmic probability paper, noted that the slopes of the curves tended to converge at four distinct points. We discussed this phenomenon and learned that four industrial hygienists had conducted the measurements. We then referred to reports of measurements made on the slides in this project from these individuals and plotted their data. Much to our surprise we were able to identify the individual by the slope of his reported data. This prompted the theory that each individual has a "limit of resolution" for a particular microscope technique.

Some of the distribution plots are presented in Figures 2, 3 and 4. For the sake of demonstration and clarity only a few of the plots of the many submitted by the observer are presented. It may be noted that the limit of resolution is not that which was calculated for the microscope. The 95× (N.A. = 1.25) was calculated to be 0.2 micron. Two plots, Figures 2 and

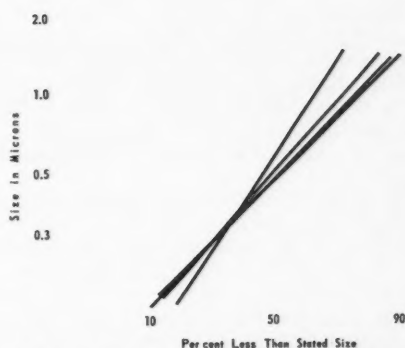


FIGURE 2. Logarithmic probability plot of particle size measurement by one examiner using microscope equipped with 30× ocular and 95× objective.

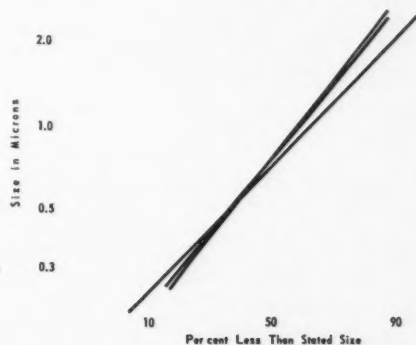


FIGURE 3. Logarithmic probability plot of particle size measurement by one examiner using microscope equipped with 10× ocular and 95× objective.



FIGURE 4. Logarithmic probability plot of particle size measurement by one examiner using microscope equipped with 10× ocular and 44× objective.

3, indicate a limit of resolution of approximately 0.3 to 0.35 micron when a 30 $\times$  compensating ocular lens was used and a limit of resolution of 0.45 when a 10 $\times$  ocular was used. The 44 $\times$  (N.A. = 0.85) was calculated to be 0.3 micron. The plot of data using this system, Figure 4, indicates a limit of resolution of approximately 0.5 micron.

The limit of resolution changes for each individual, and a review of all reports indicates that the limit of resolution decreases with practice. It should be pointed out that particle size measurements made by one person, when plotted on logarithmic probability paper, do not all converge at a single point, but enough of them will so as to indicate a probable limit of resolution.

### Summary

Particle size measurement is a major consideration for assessing the degree of hazard presented by airborne dust particulates. This paper describes a method of comparing investigators'

techniques, by re-evaluation of the same slide by a single investigator and by comparing his technique with that of his colleagues. Particle size measurement, within a reasonable degree of accuracy, depends on practice, not on general experience in the field of industrial hygiene.

An interesting observation made during this study was that of determining the limit of resolution, not only of the microscope by mathematical formulation, but of the observer. These data and the method for determining them are presented.

Data concerning the reliability of particle size measurements are also given.

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### COURSE IN INDUSTRIAL HEALTH FOR NURSES

THE DEPARTMENT OF INDUSTRIAL MEDICINE of the New York University Post-Graduate Medical School will present a full-time five-day course in industrial health for nurses beginning November 6, 1961. The course will be limited to 50 nurses engaged in industrial nursing, and will be presented under the direction of Dr. David H. Goldstein, Professor of Industrial Medicine, and the nurse faculty of the Department. Tuition will be \$60.00. Applicants should specify Course 484 and send their applications to the Dean, New York University Post-Graduate Medical School, 550 First Avenue, New York 16, New York.

Instruction will consist of lectures and conferences led by both medical and nurse faculties of the Medical Center. A field trip will permit a visit to and a study of an industrial medical department in the Greater New York Area. Several sessions will be held jointly with industrial physicians enrolled in postgraduate study. The subjects to be covered during the week include the following: Occupational Health Nursing as viewed by management, the physician and the nurse; the small plant program; communications; individual and group behavior in an industrial setting; counselling and interview techniques; legal aspects of industrial nursing; rehabilitation; preparation for retirement; and problem clinic.



# Comparative Concentration of Silica in Parent Material and in Airborne Particulate Matter

MILTON SHEINBAUM

*Division of Industrial Hygiene, New York State Department of Labor,  
80 Centre Street, New York, New York*

A comparison of the silica content of 30 airborne particulate samples from industrial exposures was made with the parent material occasioning these exposures. The data from this study indicate that in the 19 samples collected within six feet of the dust producing operation the free silica content in parent material and airborne dust were about the same. For samples collected at distances greater than six feet from the source the data are inconclusive.

THE subject of whether differences exist between the silica concentrations of airborne particulate matter in breathing zones and their proximate parent materials has been studied for some time by the New York State Department of Labor, Division of Industrial Hygiene. This report, the second to be issued, describes briefly the procedures and further preliminary results of a continuing study to determine the relationship, if any, between the silica contents of airborne particulates and parent materials.<sup>1</sup> It is intended solely to relate findings to date; no conclusions are offered.

## General Procedures

Samples of airborne and parent materials were secured by standard procedures during routine industrial hygiene investigations. Notes were made of the types of operations and their locations in relation to sampling points, and of the time spent by an operator near given operations. Airborne particulate matter was analyzed by phase microscopic procedures. Parent material samples were subjected to analyses by routine chemical methods. Standard statistical procedures were used to study results. Distance and time factors were duly considered.

## Sampling Procedures

All parent material samples were obtained as grab or ledge samples from immediate work areas. Samples of dust or small pieces of stone broken by jack hammers were taken from the immediate vicinity of drilling operations at tunnel faces or quarries. Samples were also taken from belt conveyors in stone crushing plants and

from rubble at work sites in demolition operations. Ledge samples were obtained at all grinding operations encountered and at several sand-blasting operations. In all other cases a specimen of the material being handled was used as a sample.

Air samples were collected in dust-free isopropyl alcohol or by means of Millipore field monitor membrane filter kits. In either case approximately one cubic foot of air was sampled. Midget impinger flasks operated by a hand pump for ten-minute periods were used to collect wet samples. A motor-driven pump operated for two-minute periods was used for collecting dry samples.

All samples were taken in the breathing zone of the operators in accordance with routine air sampling procedures. Table I lists the various operations sampled, the procedure used for collecting parent material samples, the media used in collecting air samples and the distance, more or less than six feet, of air sampling locations from the operations. It should be noted that two of the air samples were taken on membrane filters. Twenty-one were collected in impinger flasks and seven were obtained by a combination of both means.

Under the heading "Operation Sampled", differentiations are made between indoor and outdoor operations, between operations at which the operator stayed relatively close and those at which the operator moved about and away, and between continuous and intermittent operations. Distinctions in the latter two categories are shown simply as general air samples.

Airborne samples which had been collected in midget impinger flasks containing isopropyl al-

TABLE I  
Type of Operation and Sampling Procedure

Number	Operation Sampled	Distance Operation To Sam- pling Plus or Minus 6 Feet Location	Parent Material Sampling Procedure	Air Sampling Procedure
1-6	Outdoor, drilling city streets	-	Grab, rock chips	Impinger
7	Outdoor, quarry jack hammer	+	Grab, rock chips	Impinger
8	Outdoor, quarry wagon drill	+	Drill dust	Impinger
9	Indoors, tunnel wagon drill	-	Grab, face rock	Impinger
10	Outdoors, rock crusher	+	Grab, belt stone	Impinger
11	Outdoors, rock crusher	+	Grab, belt stone	Membrane filter
12	Outdoor & indoor, screens, belt dump	+	Grab, belt stone	Impinger
13	Indoor, belt transfer point	+	Grab, belt stone	Impinger
14	Outdoor, painting, grinding mortar joints in granite building	-	Ledge	Impinger & membrane filter
15	Indoor, demolition	-	Grab, rubble	Impinger & membrane filter
16	Indoor, demolition	-	Grab, rubble	Impinger & membrane filter
17	Outdoor, demolition (about ¼ general air)	+	Grab, rubble	Impinger & membrane filter
18	Indoor, stone sawing, about 6' from saw	-	Chip of stone being cut	Impinger & membrane filter
19	Indoor, spray plaster application	-	Grab plaster from hose	Impinger & membrane filter
20	Sand blast, unfiltered cabinet	-	Sand from cabinet	Impinger*
21	Sand blast, dirty aluminum castings	-	Sand from cabinet	Impinger
22	Strap sanding, dirty aluminum castings	-	Ledge	Impinger
23	Chipping & grinding, clean steel aluminum wheel	-	Ledge	Impinger & membrane filter
24	Weighing & dumping raw gypsum	-	Grab, from bag	Impinger
25	Weighing & dumping, silica, some room air	-	Grab, from bag	Membrane filter
26	Foundry molding	-	Ledge	Impinger
27	General air, near mica dusting	+	Grab, from bin	Impinger
28	General air, tunnel—½ to 8 miles from face	+	Grab, from truck	Impinger
29	General air, near sand mixing	+	Grab, from mixer	Impinger & membrane filter
30	General air, near tale dusting	+	Grab, from bag	Impinger

\* Sampled in fan discharge air stream.

cohol were prepared for microscopy by evaporating them completely on thin glass slides. The samples were then dyed optically in accordance with the Crossman method,<sup>2</sup> i.e., by immersion in a medium having a refractive index of 1.552-1.554. Styrene monomer or a mixture of ethyl cinnamate and butyl carbitol, compounded to a refractive index of 1.552, were used as media.

Quartzite crystals take on a deep blue color and are thus differentiated from all other materials except bi-refractive crystals which have an identical refractive index.

Quantitative estimates were made by counting several hundred particles and simultaneously differentiating and separating them in to two major groups, i.e., quartzite and non-quartzite, and further into five separate sections of particle size within each major group.

Each section comprised a size range of respectively 1 to 2, 2 to 4, 4 to 8, 8 to 16, and 16 to 32 microns. Size was estimated visually. Particles less than one micron in size were eliminated because of the inability to adequately discern true color. Those in excess of 32 microns were eliminated because they were atypical.

The number of particles in each size group was multiplied by a factor of 1, 5, 10, 20 and 40 respectively; separate totals were obtained for each major group and the percentage of quartzite was determined by establishing the proportion of quartzite to the total.

Samples obtained on membrane filters were examined directly by immersion in a mixture of ethyl cinnamate and butyl carbitol made up to a refractive index of 1.507. The counting procedure was identical to that described above.

The Talvittie method<sup>3</sup> of analysis for silica, in which phosphoric acid is used, consists of the removal of all solubles in hot orthophosphoric and fluoboric acids, followed by removal of insoluble siliceous material with hot hydrofluoric acid. The weight differential prior to and after hydrofluoric acid treatment indicates the weight of quartz.

#### Results of Analyses

Tables II and III list the percentage of free silica found in the parent material and the average percentage of free silica in all air samples taken at each location. Percentage quartzite

is assumed to indicate percentage free silica. Table II indicates the results of analyzing air samples secured at distances less than six feet from the operation. Table III shows similar data on samples secured at a greater distance. General air samples are shown separately in Table III. Figures 1 and 2 correspond to Tables II and III and show the data graphically.

The data represented in Figure 1 were analyzed statistically to determine point correlation and the linear equation showing relationship. Correlation was determined by the following equation:

$$r = \frac{N\Sigma XY - (\Sigma X)(\Sigma Y)}{[(N\Sigma X^2 - (\Sigma X)^2)(N\Sigma Y^2 - (\Sigma Y)^2)]^{1/2}}$$

where  $N$  is number of points

$\Sigma$  is % Free silica in parent material

$Y$  is % Free silica in airborne particulate matter

In solving this equation, 0.92 was established as the value for  $r$ . Attempts to correlate the data in Figure 2 failed.

The relationship between free silica concentration in the parent material and the airborne particulate was determined by simultaneously solving the following equations, having  $a$  and  $b$  as constants:

$$\Sigma Y = aN + b\Sigma X$$

$$\Sigma XY = a\Sigma X + b\Sigma X^2$$

This resulted in the relationship

$$Y = .89X + 4.4$$

#### Comments

The formation of any positive conclusions on the basis of experience with only thirty samples is not warranted; however, the arrangement of data in Figure 1 suggests that the percentage of free silica in the particulate material in the breathing zone of the worker is equal, for all practical purposes, to the percentage of free silica in the parent material. The data shown on Figure 2 are inconclusive.

#### Summary

A second progress report is presented on the relationship between the silica concentration of airborne particulate matter and the parent material from which it has been generated. Thirty airborne samples were collected using either im-

TABLE II  
Free Silica Concentration of Parent Material and Airborne Particulate Matter  
(at locations within 6 feet of the operation)

Number	% Free Silica Parent Material	% Free Silica Airborne Particulate Matter
1	49.9	34.0
2	43.6	48.5
3	36.6	33.6
4	59.6	44.5
5	33.7	35.0
6	53.7	37.8
7	13.6	35.4
9	59.0	64.0
14	39.0	36.5
16	40.1	44.9
18	29.8	48.3
19	67.8	59.6
20	72.0	93.5
21	92.9	95.7
22	3.6	7.8
23	3.1	4.6
24	0.0	2.3
25	92.2	73.3
26	14.0	15.7

TABLE III  
Free Silica Concentration of Parent Material and Airborne Particulate Matter  
(at locations more than 6 feet from the operation)

Number	% Free Silica Parent Material	% Free Silica Airborne Particulate Matter
7	13.6	35.4
8	25.7	33.8
10	6.0	18.9
11	3.9	29.1
12	11.8	29.0
13	6.4	28.4
17	69.4	33.8
General Air Samples		
27	1.3	0.4
28	44.2	2.9
29	91.8	41.7
30	1.5	23.7

pingers or membrane filters; parent materials were collected as grab or ledge samples. The Talvite method for free silica determination was used for analysis of parent materials. Phase Microscopy was used to analyze airborne particulate matter. Of the thirty sampling locations, nineteen were located within six feet of operations producing dust and eleven were located a greater distance.

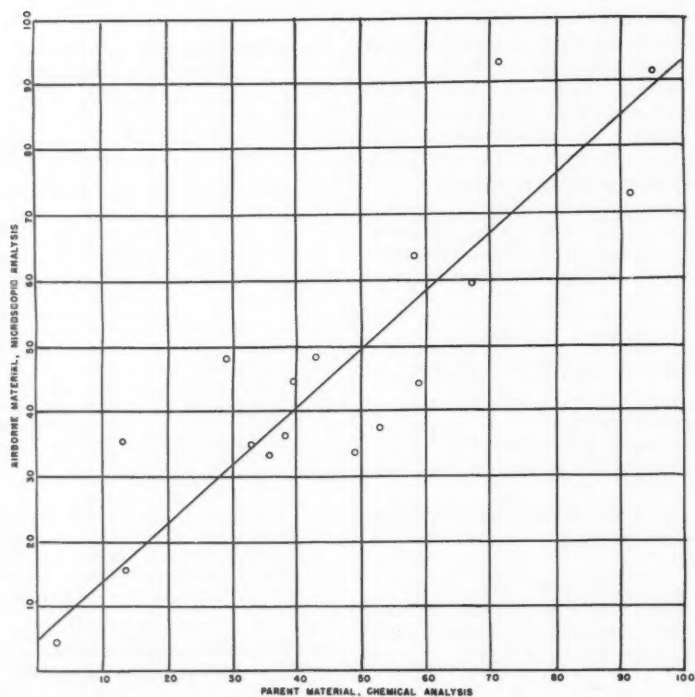


FIGURE 1. Free silica concentration of parent material and airborne particulate matter at locations within six feet of the operation.

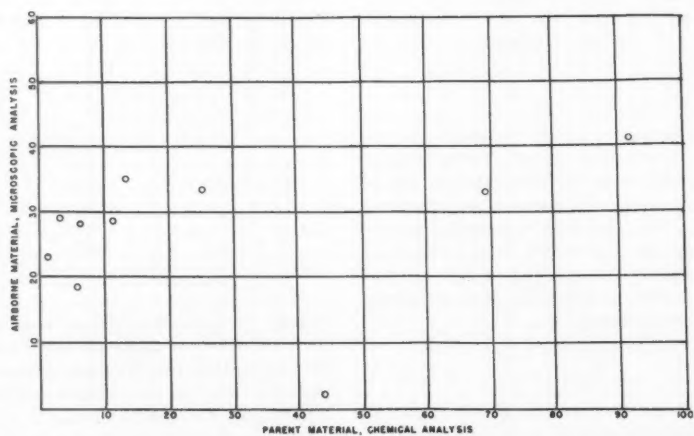


FIGURE 2. Free silica concentration of parent material and airborne particulate matter at locations greater than six feet of the operation.

Available data indicate that the concentration of free silica in the particulate matter in the breathing zone of the operator is about the same as that in the parent material in cases where operators were within 6 feet of the operation. The data are inconclusive as to relationships at distances greater than six feet.

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#### REMCAL AND REMAB

**R**ADIATION-EQUIVALENT MANIKIN, Calibration (REMCAL) and Radiation-Equivalent Manikin, Absorption (REMAB) are the names given to synthetic men whose skin and organs are made of transparent Tenite butyrate plastic and who are helping science to gauge the impact of radiation on the human body for the purpose of perfecting techniques for controlling biological applications of radiation. Vacuum-formed from the clear plastic, the body shell and other parts of these manikins permit unobstructed penetration of x-rays, gamma rays and neutrons. REMCAL has the size and contours of an average man and contains the counterparts of thyroid, liver, lungs, spleen, kidneys, and other organs, which are filled with solutions that simulate the reaction of soft human tissue when exposed to radiation. His laboratory companion, REMAB, contains in addition to its soft and hard tissue components, a complete human skeleton under the plastic shell. Ducts in the long bones of the arms and legs and in the vertebral column and in tubes that criss-cross other areas of the figure accommodate dosimeters which measure the radiation absorbed by the respective bone and body parts. Injection of radioactive solution into REMCAL's organs enables technicians to calibrate whole-body counters and other specialized instruments, and to obtain measurement data on body radiation following the application of given dosages.

These two manikins can be used in many ways to study the absorption of radiation dosages to the body and to calibrate instruments for measuring radioactive deposits in the body. Using known amounts of radioactive materials in the manikin permits calibration for various types of measurements. Both functions can be combined into one manikin if so desired. A number of these plastic men are being used in research organizations and atomic energy installations both here and abroad. Such manikins and techniques may also have applications in other areas of industrial hygiene research.



# The Efficiency of Small Gas Absorbers

SEYMOUR CALVERT and WALTER WORKMAN

*Department of Chemistry and Chemical Engineering,  
Case Institute of Technology, Cleveland 6, Ohio*

The factors affecting the efficiency of sampling for vapors by means of bubblers and absorbing solutions are discussed. A mathematical presentation of the theoretical calculations of efficiency, and formulae for practical application of calculations of efficiency are presented.

**T**HE first step in many gas analysis procedures is the collection of a gaseous pollutant from an air sample by means of a small absorber filled with an absorbing liquid. There must be some assurance that the absorption efficiency is accountable if the subsequent analytical result is to be viewed with confidence. Although the literature provides some information on specific cases, it is very desirable to have a general approach which will permit interpretation of reported results as well as providing principles for the design of new absorption systems.

A variety of absorber designs have been reported<sup>1, 2</sup> and many more are conceivable yet it is possible to deal with the majority of them in a general fashion. The simplest and most widely used absorbers involve the bubbling of the gas sample through a fixed quantity of liquid and it is this type which will be discussed here. Our objective is to present methods for predicting absorber efficiency which will be convenient and simple to use. Because of this, most of the final presentations are based on some simplifying assumptions which will be clearly stated.

As will be seen, the importance of these simplifications is minor when compared with factors dependent on the chemical nature of the system. The most desirable type of system involves a liquid constituent which reacts with the pollutant to yield a non-volatile product. The other major type involves a reversible physical absorption which results in a solution with appreciable pollutant vapor pressure. High efficiency will generally result when a sufficiently strong chemically reactive solution is used. Low efficiency will be obtained for physical absorption unless the pollutant is very soluble and the ratio of gas to liquid volume is small.

For these extremes the design of the absorber and its intrinsic efficiency are of secondary importance. In order to handle the complete range of possibilities, however, we must be able to predict:

- (1) The intrinsic efficiency or fractional approach to equilibrium ( $f$ ) for any one bubble passing through the absorber.
- (2) The average efficiency ( $F_A$ ) for the entire gas sample.

## Factors Involved in Intrinsic Efficiency

Bubbles in contact with the liquid will tend toward equilibrium with the liquid at a finite rate. After a sufficiently long time of contact equilibrium is reached and a definite mass of pollutant would have transferred from the gas to the liquid. In a short time of contact only a fraction,  $f$ , of this maximum mass would be transferred. In order to predict the amount of transfer we must first have some information regarding the physical behavior of bubbles dispersed in liquids.

Dispersion of the gas is accomplished either by introduction of a gas jet from a submerged orifice or by introduction of gas through a sintered glass plate or similar porous medium. Effective gas bubble size is practically independent of orifice (or pore) size when the bubble population is high. This observation is attributed to the coalescence of small bubbles in the vicinity of the dispersion plate. While the bubble diameters are statistically distributed, the distributions measured by Houghton et al.,<sup>3</sup> are fairly narrow and the average diameters range from 0.35 to 0.45 cm over a wide range of gas velocities. It can be seen that so far as bubble diameters are concerned there appears to be no value in using a fine fritted disc as compared with a coarse one. Although there is little information on the point, it would probably be unwise to use extremely large nozzles for dispersion. The midget impinger nozzle, for example, is about 1 mm, which provides a gas jet velocity of 6,000 cm/sec at the point of maximum absorption efficiency.

Because the extent of absorption depends on both the residence time of a bubble in the aerated column of liquid and the bubble velocity relative

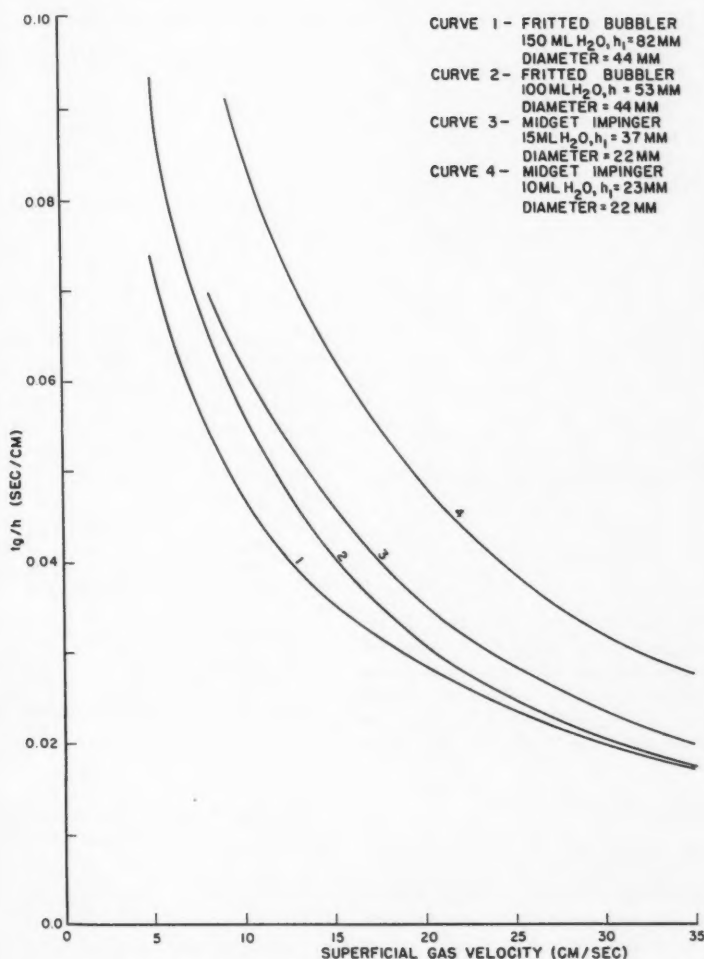


FIGURE 1.

to the liquid, it is important to have information on these quantities. Figure 1 is a plot of bubble (air) residence time per centimeter of non-aerated liquid (water) depth above the gas entrance ( $t/h_1$ ) versus superficial gas velocity ( $U_g$  - cm<sup>3</sup>/sec per cm of absorber cross-sectional area) for typical commercial absorbers.

It is noted that the quantity  $t/h_1$  is sensitive to several parameters:

- (1) Tube diameter—this is especially true for small tubes (less than 25 mm).
- (2)  $h_1$ , the original height of liquid.
- (3) The particular dispersion method used.

This latter effect is probably due in a large

measure to end effects near the gas entrance.

For any given absorber one can easily determine the quantity  $tg/h_1$  by experimental measurement. It is first necessary to note the height of unaerated liquid about the gas entrance, then measure the height of aerated liquid at the desired rate of bubbling. The quantity  $tg/h_1$  can then be calculated from:

$$t_0/h_1 = \frac{1 - h_1/h_2}{(h_1/h_2) U_g}$$

The velocity of rise of single bubbles<sup>4</sup> is

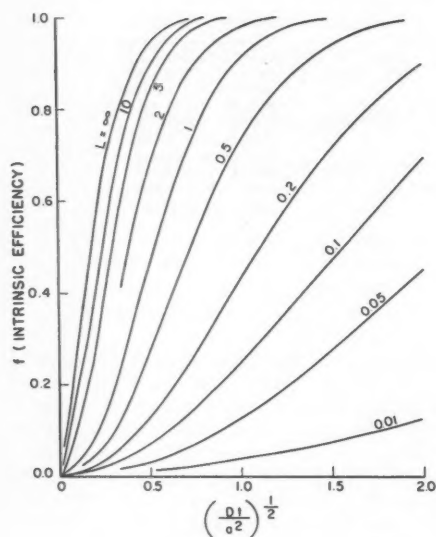


FIGURE 2.

roughly constant at 24 cm/sec for bubble diameters greater than 0.2 cm. While the average velocity relative to the absorber walls is lower than this where bubble population is high, we will approximate the velocity relative to the liquid as being equal to the velocity of rise of a single bubble.

#### Transfer from Bubbles

We may set a lower limit for the rate of mass transfer from bubbles to the gas-liquid interface by considering the process to involve only molecular diffusion from a stagnant sphere even though gas circulation within the bubble would increase the rate. The transfer rate from the interface into the liquid is given fairly well by Higbie's penetration theory as:

$$k_L = \sqrt{\frac{2D_L u_B}{\pi a}}$$

The time of contact or surface renewal is taken as  $(2a/u_B)$ , the time required for a bubble to rise through one diameter of height.

If it is assumed that each bubble contacts liquid of constant average composition during its entire period of rise, we may use the solution given by Crank<sup>6</sup>

$$f = 1 - \sum_{n=1}^{\infty} \frac{6L^2 e^{-\beta_n^2 (D_g t/a^2)}}{\beta_n^2 [\beta_n^2 + L(L-1)]} \quad (2)$$

where  $\beta_n$ 's are the roots of

$$\beta_n \cot \beta_n + L - 1 = 0 \quad (2a)$$

and

$$L = \frac{aRTk_L}{HD_g} \quad (2b)$$

This solution is presented graphically in Figure 2, a plot of  $f$  versus

$$\sqrt{\frac{D_g t}{a^2}}$$

with  $L$  as parameter. We may note that for  $L$  greater than about 30 the gas phase resistance controls and for  $L$  less than about 0.3 the liquid phase resistance controls. It will now be demonstrated that the principal factor which determines the controlling phase (and thereby the efficiency) is the solubility constant,  $H$ .

Let us assume that

- (1) Average bubble radius,  $a$ , is 0.2 cm and average velocity of rise,  $u_B$ , is 24 cm/sec.
- (2) Average gas diffusivity,  $D_g$ , is 0.1 cm<sup>2</sup>/sec and average liquid diffusivity,  $D_L$ , is  $1.5 \times 10^{-6}$  cm<sup>2</sup>/sec.
- (3) Temperature,  $T$ , is 298°K.
- (4) Absorption liquid is a dilute aqueous solution. (This is implicit in 1 and 2, above).

Upon making these substitutions we have:

$$L = \frac{1,665}{H} \quad (3)$$

The dependence of efficiency on  $H$  is illustrated in Figure 3, a plot of  $f$  versus  $H$  with

$$\sqrt{\frac{D_g t}{a^2}}$$

as parameter. An "average" absorber might have an unaerated liquid height of about 5 cm and a gas contact time of about 0.22 sec. so that

$$\frac{D_g t}{a^2} \approx 0.75.$$

From Figure 3 we can see that the efficiency of an "average" absorber for a moderately soluble gas such as CO<sub>2</sub> ( $H > 10,000$ ) would be quite low.

#### Effect of Chemical Reaction

We have seen that where solubility is low the intrinsic efficiency is low because liquid phase resistance controls and liquid diffusivities are much lower than gas diffusivities. It will also be shown later that where solubility is low the equilibrium limit on efficiency becomes severe. Thus there are

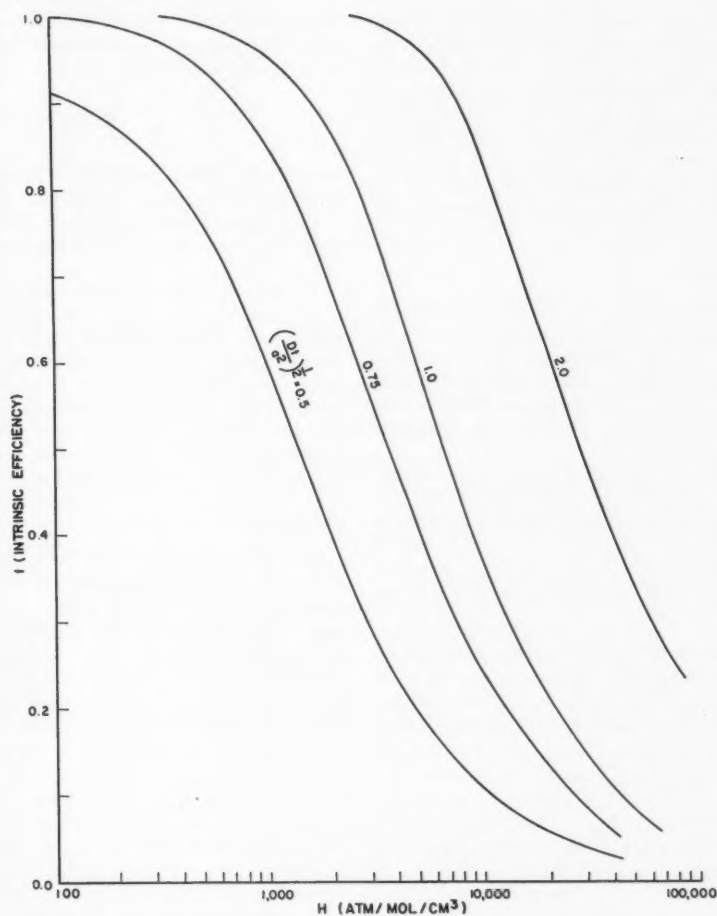


FIGURE 3.

two good reasons for using a chemically reactive solution to reduce the equilibrium pressure (raise the solubility) of the absorbed gas above the liquid.

Although the reaction products might be non-volatile, there is still no assurance that liquid phase resistance will be negligible. It is necessary that the reacting substance diffuse through the liquid toward the gas-liquid interface and react at a high enough rate to match the rate of diffusion of the pollutant into the liquid. If reactant diffuses to the interface too slowly or if the reaction rate is too low the reaction zone will be displaced a considerable distance into the liquid with the result that the interface is depleted of reactant and no benefit is obtained.

The situation of greatest interest is that where a very rapid second order reaction yields a non-volatile product. For the approximation that the diffusivities of pollutant and reactant are equal we may use the solution given by Sherwood and Pigford:<sup>6</sup>

$$k_L = \left(1 + \frac{q}{C_{Ai}}\right) \sqrt{\frac{2D_L u_B}{\pi a}} \quad (4)$$

where  $C_{Ai}$  is the concentration of the pollutant in the liquid at the interface and  $q$  is the concentration of reactant in the bulk of the liquid.

It can be seen that if the ratio  $(q/C_{Ai})$  is low, equation 4 becomes identical with equation 1 for physical absorption. In view of the assumptions

made in deriving equation 4, it can only be considered to give an approximate indication of the effect of reactant concentration relative to pollutant concentration. For practical use, however, it is quite adequate for setting the order of magnitude of the minimum reactant concentration required to reduce liquid phase resistance. The criterion to use is whether  $L$ , as evaluated by equation 2b, is high enough for satisfactory efficiency.

#### Equilibrium Limit

Up to this point we have been concerned with factors determining the fractional approach to equilibrium. Where a chemically reactive solution yields a non-volatile product this is all we need. For the case of physical absorption, however, the efficiency limit imposed by equilibrium considerations is most important.

If the effect of increasing liquid phase concentration of pollutant is taken into account, the average overall efficiency from time = 0 to time =  $t_a$  is given by:

$$F_a = \frac{V_L RT}{H G t_a} [1 - e^{-f(H G t_a / V_L R T)}] \quad (5)$$

For any particular system and temperature the only variable is the ratio of gas sample volume to liquid volume ( $G t_a / v_L$ ); which, for convenience will be called " $r_s$ ". The effect of the equilibrium

limit is shown in Figure 4, a plot of  $F_a$  versus  $(H r_s / RT)$  with  $r_s$  as parameter. Values of " $f$ " were taken from Figure 3 for

$$\sqrt{\frac{D_c t}{a^2}} = 0.75$$

and " $T$ " was taken as 293°K. For common situations where  $r_s$  might be 100 or more the efficiency is determined almost entirely by the equilibrium limit which can be computed by means of equation 5 with  $f = 1.0$ .

We may note from Figure 4 that for an "average" absorption system the overall efficiency will be only slightly affected by the intrinsic efficiency. This is shown more clearly by Figure 5, a plot of  $F_a$  versus  $H$  with  $r_s$  as the parameter and for the same "average" conditions as Figure 4. The gas to liquid ratio,  $r_s$ , must be extremely low before the overall efficiency approaches the intrinsic efficiency shown by the line for  $f = F_a$ .

#### Discussion

The methods which have been presented are sufficient for estimating collection efficiencies for most practical purposes. Results of essentially the same methods for treating physical absorption and absorption with chemical reaction have been compared with experimental data by the authors in a previous paper.<sup>7</sup> Experimental confirmation of the treatment of the equilibrium limited case

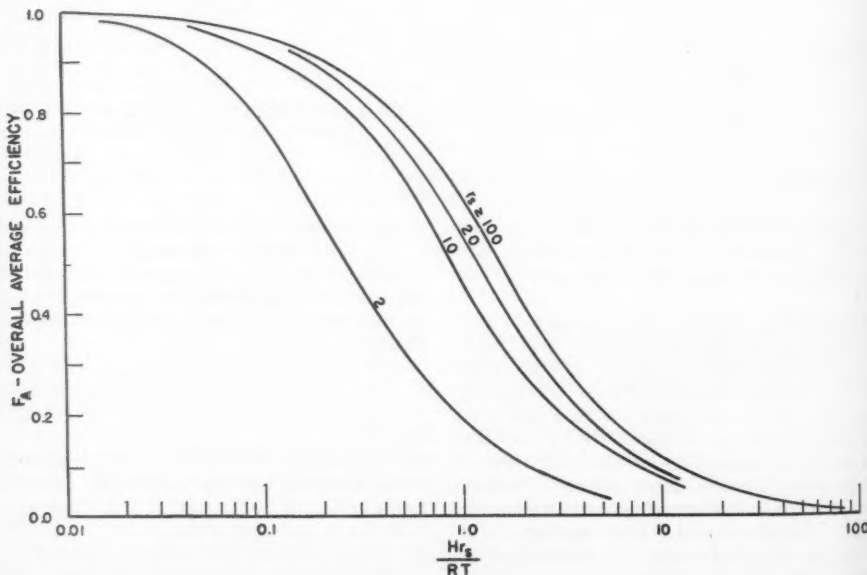


FIGURE 4.



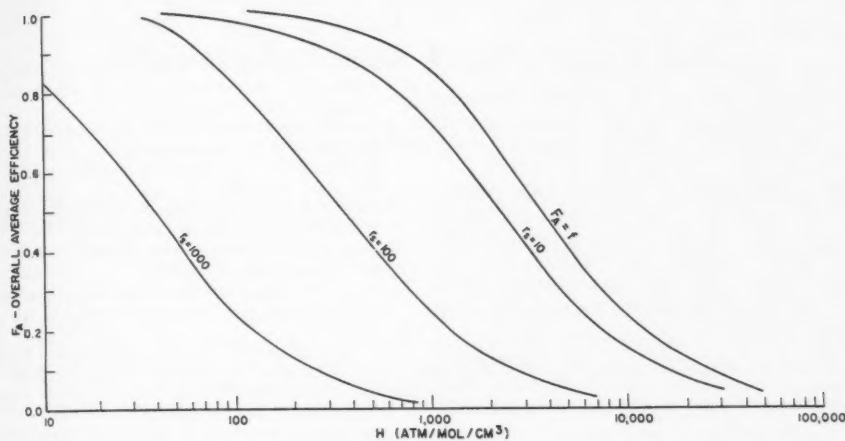


FIGURE 5.

was presented by Gage.<sup>8</sup> We may conclude from these that while the actual physical situation is more complex than was assumed in deriving the equations, the accuracy of prediction remains adequate for most practical situations.

Where very precise knowledge of absorption efficiency is required it is necessary to determine it experimentally. Also, there are some systems such as ammonia absorption in water where effects such as interfacial resistance or unforeseen liquid phase reactions may be significant although not accounted for unless specific information is available. The authors have demonstrated<sup>7</sup> that the results of Roberts and McKee<sup>9</sup> for ammonia absorption by water in several types of small absorbers can be reconciled with results obtained in large industrial absorbers. Such phenomena as internal circulation in the bubbles or concurrent flow of the liquid may also have considerable effect on efficiency. In general, however, one will have either an equilibrium limited case, which is fairly insensitive to intrinsic efficiency, or a chemical reaction case, which can be made very efficient by using proper concentration and a commonly good absorber.

#### Procedure

Predictions of efficiency for systems operating at room temperature and atmospheric pressure and with a dilute aqueous liquid can be estimated by means of Figures 3 and 4 for physical absorption. For more accurate predictions or for unusual conditions of temperature, pressure, or liquid viscosity, Figures 1 and 2 and equations 1, 2b and 5 must be used. Data on diffusivities and other physical properties may be found in sources such as the *International Critical Tables*, chemistry

handbooks, and *The Properties of Gases and Liquids* by Reid and Sherwood. Methods for predicting diffusivities and other properties where data are not available or where data must be extrapolated are presented by Reid and Sherwood.

For cases of chemical reaction other than the second order, infinitely rapid, irreversible type, one may consult Dankwerts,<sup>10</sup> van Krevelen and Hoftyzer,<sup>11</sup> and Sherwood and Pigford<sup>6</sup> for suitable definitions of  $k_L$ . Where the second order, rapid, irreversible type applies the conservative approach is to evaluate  $C_{Ai}$  as that concentration which is in equilibrium with the inlet gas. The ratio  $(q/C_{Ai})$  should be in terms of equivalents. That is, the ratio in molar concentrations should be multiplied by the ratio of moles of pollutant combining with a mole of reactant.

The most reliable predictions are those for the equilibrium limited case ( $r$ , greater than about 100). For other cases the efficiency must be checked experimentally.

#### Definitions of Symbols

- $A$  = Designation of transferring component
- $a$  = Bubble radius (cm)
- $C_a$  = Average concentration of  $A$  in liquid at any instant (mol/cm<sup>3</sup>)
- $C_{Ai}$  = Concentration of  $A$  in the liquid interface (mol/cm<sup>3</sup>)
- $D_o$  = Gas-phase diffusivity (cm<sup>2</sup>/sec)
- $D_L$  = Liquid-phase diffusivity (cm<sup>2</sup>/sec)
- $F_A$  = Overall average collection efficiency
- $f$  = Fractional instantaneous approach to equilibrium =  $\frac{p_1 - p_2}{p_1 - HC_a}$  = equilibrium collection efficiency
- $G$  = Gas flow rate (cm<sup>3</sup>/sec)

- $H$  = Henry's Law Constant  $\left(\frac{\text{atm}}{\text{mol/cm}^3}\right)$   
 $h_1$  = Liquid depth before aeration  
 $k_L$  = Liquid phase mass transfer coefficient  
 (mols/cm<sup>2</sup>-sec-mol/cm<sup>3</sup>) based on driving  
 force  $-(C_{Ai} - C_a)$   
 $L$  = Parameter, see equation 2b  
 $p_1$  = Partial pressure of  $A$  in inlet gas (atm)  
 $p_2$  = Partial pressure of  $A$  in outlet gas (atm)  
 $p_e$  = Partial pressure of  $A$  in equilibrium with  
 liquid concentration,  $C_a$  (atm)  
 $q$  = Concentration (average) of  $B$  in liquid for  
 one mole of  $B$  reacting with one mole of  $A$   
 (mol/cm<sup>3</sup>)  
 $R$  = Gas law constant =  $82.057 \left(\frac{\text{atm} - \text{cm}^3}{\text{mol} - ^\circ\text{K}}\right)$   
 $r_s$  = Ratio of total gas volume sampled to li-  
 quid volume  
 $T$  = Absolute temperature ( $^\circ\text{K}$ )  
 $t_g$  = Residence time of a gas bubble (sec)  
 $u_B$  = Bubble velocity relative to liquid (cm/sec)  
 $u_g$  = Superficial gas velocity (cm<sup>3</sup>/min-cm<sup>2</sup>)  
 $V_L$  = Volume of liquid in absorber (cm<sup>3</sup>)  
 $\pi$  = 3.1416

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## COURSE IN AIR POLLUTION

THE PUBLIC HEALTH SERVICE, through its Division of Air Pollution, will present a 1-week training course, "Medical and Biological Aspects of Air Pollution," December 11-15, 1961, at Cincinnati, Ohio, for physicians and other scientific personnel engaged in or responsible for studies of health-related effects of air pollution. The course reviews air pollution fundamentals (sources, engineering, chemical methods of assessment, meteorology, and control procedures) and considers the health effects and biological damage resulting from air pollution, the experimental evidence on animals (including animal research and laboratory methodology) and experimental studies with humans, maximum permissible concentrations for substances vented into the outdoor air, and associated legal and administrative problems.

Full description of the course is given in the *Training Program Bulletin* which is available on request. Address applications for the course or requests for information to the Chief, Training Program, Robert A. Taft Sanitary Engineering Center, 4676 Columbia Parkway, Cincinnati 26, Ohio, or to a PHS Regional Office.

## Threshold Limit Values for 1961

*Adopted at the 23rd Annual Meeting of the American Conference of Governmental Industrial Hygienists, Detroit, Michigan, April 9-12, 1961.*

Threshold limits should be used as guides in the control of health hazards and should not be regarded as fine lines between safe and dangerous concentrations. They represent conditions under which it is believed that nearly all workers may be repeatedly exposed, day after day, without adverse effect. The values listed refer to time-weighted average concentrations for a normal workday. The amount by which these figures may be exceeded for short periods without injury to health depends upon a number of factors such as the nature of the contaminant, whether very high concentrations even for short periods produce acute poisoning, whether the effects are cumulative, the frequency with which high concentrations occur, and the duration of such periods. All must be taken into consideration in arriving at a decision as to whether a hazardous situation exists. Special consideration should be

given to the application of these values in assessing the health hazards which may be associated with exposure to combinations of two or more substances.

Threshold limits are based on the best available information from industrial experience, from experimental studies, and, when possible, from a combination of the two. These values are based on various criteria of toxic effects or on marked discomfort; thus, they should not be used as a common denominator of toxicity, nor should they be considered as the sole criterion in proving or disproving diagnosis of suspected occupational disease.

These limits are intended for use in the field of industrial hygiene and should be employed by persons trained in this field. They are not intended for use, or for modification for use, in the evaluation or control of community air pollution or air pollution nuisances.

These values are reviewed annually by the Committee on Threshold Limits for changes, revisions, or additions as further information becomes available. The Committee welcomes the suggestion of substances to be added to the list and also comments, references, or reports of experience with these materials.

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## Recommended Values

## GASES AND VAPORS

Substance	P.P.M.*	Approx. Mg. per Cu. M.†
Acetaldehyde.....	200	360
Acetic acid.....	10	25
Acetic anhydride.....	5	20
Acetone.....	1,000	2,400
Acetylene tetrabromide.....	1	14
Acrolein.....	0.5	1.2
Acrylonitrile—Skin.....	20	45
Allyl alcohol—Skin.....	2	5
Allyl chloride.....	5	13
Allyl propyl disulfide.....	2	12
Ammonia.....	100	70
Amyl acetate.....	200	1,050
Amyl alcohol (isoamyl alcohol).....	100	360
Aniline—Skin.....	5	19
Arsine.....	0.05	0.2
Benzene (benzol).....	25	80
Benzyl chloride.....	1	5
Boron trifluoride.....	1	3
Bromine.....	0.1	0.7
Butadiene (1,3-butadiene).....	1,000	2,200
2-Butanone (methyl ethyl ketone).....	200	590
Butyl acetate (n-butyl acetate).....	200	950
Butyl alcohol (n-butanol).....	100	300
tert. Butyl alcohol.....	100	300
Butylamine.....	5	15
Butyl cellosolve (2-butoxyethanol).....	50	240
p-tert. Butyltoluene.....	10	60
Carbon dioxide.....	5,000	9,000
Carbon disulfide—Skin.....	20	60
Carbon monoxide.....	100	110
Carbon tetrachloride—Skin.....	25	160
Cellosolve (2-ethoxyethanol).....	200	740
Cellosolve acetate (2-ethoxyethyl acetate).....	100	540
Chlorine.....	1	3
Chlorine dioxide.....	0.1	0.3
Chlorine trifluoride.....	0.1	0.4
Chlorobenzene (monochlorobenzene).....	75	350
Chloroform (trichloromethane).....	50	240
1-Chloro-1-nitropropane.....	20	100
Chloropicrin.....	0.1	0.7
Chloroprene (2-chloro-1,3-butadiene).....	25	90
Cresol (all isomers)—Skin.....	5	22
Cyclohexane.....	400	1,400
Cyclohexanol.....	50	200
Cyclohexanone.....	50	200
Cyclohexene.....	400	1,350
Decaborane—Skin.....	0.05	0.3
Diacetone alcohol (4-hydroxy-4-methyl-2-pentanone).....	50	240
Diborane.....	0.1	0.1
o-Dichlorobenzene.....	50	300
p-Dichlorobenzene.....	75	450
Dichlorodifluoromethane.....	1,000	4,950
1,1-Dichloroethane.....	100	400
1,2-Dichloroethane (ethylene dichloride).....	100	400
1,2-Dichloroethylene.....	200	790
Dichloroethyl ether.....	15	90
Dichloromono-fluoromethane.....	1,000	4,200
1,1-Dichloro-1-nitroethane.....	10	60
Dichlorotetrafluoroethane.....	1,000	7,000

## GASES AND VAPORS—Continued

Substance	P.P.M.*	Approx. Mg. per Cu. M.†
Diethylamine.....	25	75
Difluorodibromomethane.....	100	860
Diisobutyl ketone.....	50	290
Dimethylaniline (N-dimethylaniline)—Skin.....	5	25
Dimethylformamide.....	20	60
1,1-Dimethylhydrazine—Skin.....	0.5	1
Dimethylsulfate—Skin.....	1	5
Dipropylene glycol methyl ether.....	100	600
Dioxane (diethylene dioxide).....	100	360
Ethyl acetate.....	400	1,400
Ethyl acrylate—Skin.....	25	100
Ethyl alcohol (ethanol).....	1,000	1,900
Ethylamine.....	25	45
Ethylbenzene.....	200	870
Ethyl bromide.....	200	890
Ethyl chloride.....	1,000	2,600
Ethyl ether.....	400	1,200
Ethyl formate.....	100	300
Ethyl silicate.....	100	850
Ethylene chlorohydrin—Skin.....	5	16
Ethylenediamine.....	10	30
Ethylene dibromide (1,2-dibromoethane).....	25	190
Ethylene imine—Skin.....	5	9
Ethylene oxide.....	50	90
Fluorine.....	0.1	0.2
Fluorotrichloromethane.....	1,000	5,900
Formaldehyde.....	5	6
Furfural.....	5	20
Furfuryl alcohol.....	50	200
Gasoline.....	500	2,000
Heptane (n-heptane).....	500	2,000
Hexane (n-hexane).....	500	1,800
Hexanone (methyl butyl ketone).....	100	410
Hexone (methyl isobutyl ketone).....	100	410
Hydrazine—Skin.....	1	1.3
Hydrogen bromide.....	3	10
Hydrogen chloride.....	5	7
Hydrogen cyanide—Skin.....	10	11
Hydrogen fluoride.....	3	2
Hydrogen peroxide, 90%.....	1	1.4
Hydrogen selenide.....	0.05	0.2
Hydrogen sulfide.....	20	30
Iodine.....	0.1	1
Isophorone.....	25	140
Isopropylamine.....	5	12
Mesityl oxide.....	25	100
Methyl acetate.....	200	610
Methyl acetylene.....	1,000	1,650
Methyl acrylate—Skin.....	10	35
Methylal (dimethoxymethane).....	1,000	3,100
Methyl alcohol (methanol).....	200	260
Methyl bromide—Skin.....	20	80
Methyl cellosolve (2-methoxyethanol).....	25	80
Methyl cellosolve acetate (ethylene glycol monomethyl ether acetate).....	25	120
Methyl chloride.....	100	210
Methyl chloroform (1,1,1-trichloroethane).....	500	2,700
Methyleyclohexane.....	500	2,000
Methyleyclohexanol.....	100	470
Methyleyclohexanone.....	100	460

Note: The word "Skin" following a compound's name indicates that the liquid compound can penetrate the skin to cause systemic effects.

## GASES AND VAPORS—Continued

Substance	P.P.M.*	Approx. Mg. per Cu. M.†
Methyl formate.....	100	250
Methylisobutyl carbinol (methyl amyl alcohol).....	25	100
$\alpha$ -Methyl styrene.....	100	480
Methylene chloride (dichloromethane).....	500	1,750
Monomethyl aniline—Skin.....	2	9
Naphtha (coal tar).....	200	800
Naphtha (petroleum).....	500	2,000
Nickel carbonyl.....	0.001	0.007
Nitric acid.....	10	25
<i>p</i> -Nitroaniline—Skin.....	1	6
Nitrobenzene—Skin.....	1	5
Nitroethane.....	100	310
Nitrogen dioxide.....	5	9
Nitroglycerin.....	0.5	5
Nitromethane.....	100	250
2-Nitropropane.....	25	90
Nitrotoluene—Skin.....	5	30
Octane.....	500	2,350
Ozone.....	0.1	0.2
Pentane.....	1,000	2,950
Pentanone (methyl propyl ketone).....	200	700
Perchloroethylene (tetrachloroethylene).....	100	670
Phenol—Skin.....	5	19
Phenylhydrazine—Skin.....	5	22
Phosgene (carbonyl chloride).....	1	4
Phosphine.....	0.05	0.07
Phosphorus trichloride.....	0.5	3
Propyl acetate.....	200	840
Propyl alcohol (isopropyl alcohol).....	400	980
Propyl ether (isopropyl ether).....	500	2,100
Propylene dichloride (1,2-dichloropropane).....	75	350
Propylene imine—Skin.....	25	60
Propylene oxide.....	100	240
Pyridine.....	5	15
Quinone.....	0.1	0.4
Stibine.....	0.1	0.5
Stoddard solvent.....	500	2,900
Styrene monomer (phenylethylene).....	100	420
Sulfur dioxide.....	5	13
Sulfur hexafluoride.....	1,000	6,000
Sulfur monochloride.....	1	6
Sulfur pentafluoride.....	0.025	0.25
1,1,2,2-Tetrachloroethane—Skin.....	5	35
Tetrahydrofuran.....	200	590
Tetranitromethane.....	1	8
Toluene (toluol).....	200	750
<i>o</i> -Toluidine—Skin.....	5	22
Toluene-2,4-diisocyanate.....	0.02‡	0.14‡
Trichloroethylene.....	100	520
Triethylamine.....	25	100
Trifluoromonomobromomethane.....	1,000	6,100
Turpentine.....	100	560
Vinyl chloride (chloroethylene).....	500	1,300
Vinyl toluene.....	100	480
Xylene (xylo).....	200	870
Xylidine—Skin.....	5	25

\* Parts of vapor or gas per million parts of air by volume at 25° C and 760 mm. Hg pressure.

† Approximate milligrams per cubic meter of air.

‡ Probably sufficiently low to protect against primary sensitization, but may not protect persons specifically sensitized.

## DUST, FUMES AND MISTS

Substance	Mg. per Cu. M.‡
Aldrin (1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4,5,8-dimethanonaphthalene)—Skin.....	0.25
Ammonate (ammonium sulfamate).....	15
Antimony.....	0.5
ANTU (alpha-naphthyl-thiourea).....	0.3
Arsenic.....	0.5
Barium (soluble compounds).....	0.5
Beryllium.....	0.002
Cadmium oxide fume.....	0.1
Calcium arsenate.....	0.1
Chlordane (1,2,4,5,6,7,8,8-octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane).....	2
Chlorinated camphene, 60%.....	0.5
Chlorinated diphenyl oxide.....	0.5
Chlorodiphenyl (42% chlorine)—Skin.....	1
Chlorodiphenyl (54% chlorine)—Skin.....	0.5
Chromic acid and chromates (as CrO <sub>3</sub> ).....	0.1
Crag herbicide (sodium 2-[2,4-dichlorophenoxy] ethanol hydrogen sulfate).....	15
Cyanide (as CN)—Skin.....	5
2,4-D (2,4-dichlorophenoxyacetic acid).....	10
DDT (2,2-bis [p-chlorophenyl]-1,1,1-trichloroethane).....	1
Dieldrin (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4,5,8-dimethanonaphthalene)—Skin.....	0.25
Dinitrobenzene—Skin.....	1
Dinitrotoluene—Skin.....	1.5
Dinitro- <i>o</i> -cresol—Skin.....	0.2
EPN (O-ethyl O- <i>p</i> -nitrophenyl thionobenzene-phosphonate)—Skin.....	0.5
Ferbam (ferric dimethyl dithiocarbamate).....	15
Ferrovanadium dust.....	1
Fluoride.....	2.5
Hydroquinone.....	2
Iron oxide fume.....	15
Lead.....	0.2
Lead arsenate.....	0.15
Lindane (hexachlorocyclohexane, gamma isomer).....	0.5
Lithium hydride.....	0.025
Magnesium oxide fume.....	15
Malathion (O,O-dimethyl dithiophosphate of diethyl mercaptosuccinate)—Skin.....	15
Manganese.....	5
Mercury.....	0.1
Mercury (organic compounds)—Skin.....	0.01
Methoxychlor (2,2-di- <i>p</i> -methoxyphenyl-1,1,1-trichloroethane).....	15
Molybdenum (soluble compounds).....	5
(insoluble compounds).....	15
Nicotine—Skin.....	0.5
Parathion (O,O-diethyl-O- <i>p</i> -nitrophenyl thiophosphate)—Skin.....	0.1
Pentachloronaphthalene—Skin.....	0.5
Pentachlorophenol—Skin.....	0.5
Phosphoric acid.....	1
Phosphorus (yellow).....	0.1
Phosphorus pentachloride.....	1
Phosphorus pentasulfide.....	1
Picric acid—Skin.....	0.1
Pyrethrum.....	2
Rotenone.....	5
Selenium compounds (as Se).....	0.1
Sodium fluoroacetate (1080)—Skin.....	0.1



## DUST, FUMES AND MISTS—Continued

Substance	Mg. per Cu. M. §
Sodium hydroxide.....	2
Strychnine.....	0.15
Sulfuric acid.....	1
TEDP (tetraethyl dithionopyrophosphate)—Skin.....	0.2
TEPP (tetraethyl pyrophosphate)—Skin.....	0.05
Tellurium.....	0.1
Tetryl (2,4,6-trinitrophenylmethylnitramine)—Skin.....	1.5
Thallium (soluble compounds).....	0.1
Thiram (tetramethyl thiuram disulfide).....	5
Titanium dioxide.....	15
Trichloronaphthalene—Skin.....	5
Trinitrotoluene—Skin.....	1.5
Uranium (soluble compounds).....	0.05
(insoluble compounds).....	0.25
Vanadium (V <sub>2</sub> O <sub>5</sub> dust).....	0.5
(V <sub>2</sub> O <sub>5</sub> fume).....	0.1
Warfarin (3-[ $\alpha$ -acetylbenzyl]-4-hydroxycoumarin).....	0.5
Yttrium.....	5
Zinc oxide fume.....	15
Zirconium compounds (as Zr).....	5

§ Milligrams of dust, fume, or mist per cubic meter of air.

Radioactivity: For permissible concentrations of radioisotopes in air, see U. S. Department of Commerce, National Bureau of Standards, Handbook 69, "Maximum Permissible Body Burdens and Maximum Permissible Concentrations of Radionuclides in Air and in Water for Occupational Exposure", June 5, 1959. Also, see U. S. Department of Commerce, National Bureau of Standards, Handbook 59, "Permissible Dose from External Sources of Ionizing Radiation", September 24, 1954, and addendum of April 15, 1958.

## MINERAL AND NON-METALLIC INORGANIC DUSTS

Substance	M.P.P.C.F.
Silica	
Quartz	
High (above 50% free silica).....	5
Medium (5 to 50% free silica).....	20
Low (below 5% free silica).....	50
Cristobalite (above 5%).....	5
Amorphous.....	20
Silicates	
Asbestos.....	5
Mica.....	20
Portland Cement.....	50
Soapstone.....	20
Talc.....	20
Miscellaneous:	
Aluminum Oxide.....	50
Calcite.....	50
Dolomite.....	50
Limestone.....	50
Marble.....	50
Silicon Carbide.....	50
Other inert dusts.....	50

|| Millions of particles per cubic foot of air based on impinger samples counted by light-field techniques.

## TENTATIVE VALUES

Substance	P.P.M. ¶	Approx. Mg. per Cu. M. ¶¶
Acetonitrile.....	40	70
Allyl glycidyl ether (AGE).....	10	45
Boron oxide.....		15
tert. Butyl chromate (as CrO <sub>3</sub> ).....		0.1
n-Butyl glycidyl ether (BGE).....	50	270
Butyl mercaptan.....	10	35
Chloroacetaldehyde.....	1	3
Chlorobromomethane.....	200	1,080
DDVP (O,O-Dimethyl-2,2-Dichlorodimethyl phosphate).....		1
Diglycidyl ether (DGE).....	10	55
Dimethyl acetamide.....	10	35
Endrin (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octa hydro-1,4-endo, endo-5,8-dimethano-naphthalene).....		0.25
Ethanol amine.....	0.5	1
Ethyl mercaptan.....	250	640
Glycidol.....	50	150
Heptachlor (1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene).....		0.25
sec-Hexyl acetate.....	100	590
Isopropyl glycidyl ether (IGE).....	50	240
Ketene.....	0.5	0.9
Methyl mercaptan.....	50	100
1-Nitropropane.....	25	90
Pentaborane.....	0.005	0.01
Perchloromethyl mercaptan.....	0.1	0.5
Phenyl glycidyl ether (PGE).....	50	310
Phosdrin (2-carbomethoxy-1-methyl vinyl dimethyl phosphate).....		0.1
n-Propyl nitrate.....	25	110
Systox.....		0.2
2,4,5T (2,4,5-trichlorophenoxy acetic acid).....		10
Teflon decomposition products (as F).....		0.05
1,2,3-Trichloropropane.....	50	300
1,1,2-Trichloro-1,2,2-trifluoroethane.....	1,000	7,600
Triorthocresyl phosphate.....		0.1
Triphenyl phosphate.....		3

¶ Parts of vapor or gas per million parts of air by volume at 25° C and 760 mm. Hg pressure.

¶¶ Approximate milligrams per cubic meter of air.

William L. Ball      Hervey B. Elkins  
W. Clark Cooper      Russel G. Scovill  
Herbert E. Stokinger      William F. Reindollar  
Keith H. Jacobson      Allan L. Coleman, Chairman

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